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The Absorption Spectrum of Acetone Vapor in the Far Ultraviolet

A. B. F. DUNCAN, *Department of Chemistry, Brown University*
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The absorption spectrum of acetone has been photographed down to 850A. Discrete bands were found above 1300A but only continuous absorption between 1300 and 850A. The bands are described and a qualitative interpretation is given of the complete spectrum. One Rydberg series was found, converging to an ionization potential of 10.20 volts.

THERE are few molecules whose spectra are known in frequency ranges which are wide enough to include all electronic states giving discrete absorption. The absorption spectrum of acetone down to 1800A was recently reported,[1] and a detailed description of the first two stable excited states given. The spectrum of this molecule has now been extended down to 850A. Since only continuous absorption exists from about 1300A down to this lower limit, it is quite possible that no discrete absorption will appear at shorter wavelengths, and that all the stable states are indicated in the data presented here.

The spectra were taken from a one meter focus glass grating used at normal incidence, with a theoretical resolving power of 120,000. The spectrograph was evacuated with a high speed diffusion pump using Apiezon Oil B, backed by a Cenco Hypervac pump. Eastman III–0 plates, sensitized with Nujol oil were used. The light source was a condensed discharge in hydrogen, described previously. The spectrograph, giving an absorbing column of about two meters, was filled with acetone at pressures from 0.0025 to 0.15. It was necessary to take plates at frequent pressure intervals over this range. No new bands appeared, however above 0.035 mm pressure. The highly purified acetone was that used in the previous work.

The following lines were used as wavelength standards: 1066.555 (Si IV), 1215.68 (H, in absorption), 1388.66 (O IV), 1548. 189 (C), and 1550.774 (C). The dispersion, 8.532 A/mm, was effectively constant over the range used.

The bands with sharp edges could be measured to 0.05–0.08A. The moderately diffuse bands could be measured with about half the above accuracy. A few were too diffuse to measure at all, and so cannot be reported. Five final plates showing twenty independent spectra were measured. The majority of the bands were measured independently five to ten times. The average deviation from the mean in measurement, expressed in wave numbers is 5 or less for the sharp bands and 5 to 15 for the diffuse bands. The bands observed are listed in Table I. All bands not labeled *s* are more or less diffuse. The intensities were estimated visually and checked by two other observers.

[1] Noyes, Duncan and Manning, J. Chem. Phys. **2**, 717 (1934).

TABLE I. *Acetone bands 1800–850A.*

Frequency (cm^{-1})	Intensity	Lowest pressure obs. (mm Hg)	Frequency (cm^{-1})	Intensity	Lowest pressure obs. (mm Hg)
60086 *s*	2	0.0125	69316 *s*	3	0.0125
60361	0	0.035	70000	4	0.0125
60644	0	0.028	71096	2	0.0125
61122	1	0.02	71308 *s*	6	0.0125
61361	1	0.0125	71485 *s*	6	0.0125
61548	0	0.035	71634	1	0.0125
62201 *s*	3	0.0125	72529	4	0.0025
62406	0	0.028	73834 *s*	8	0.005
62529	3	0.0125	74150	4	0.0125
63019	2	0.0125	75376 *s*	8	0.005
63255	3	0.0125	75575	1	0.005
63576	2	0.005	75872	1	0.005
63847	2	0.0125	76030 *s*	8	0.0125
65213 *s*	10	0.0025	76563 *s*	4	0.0125
65563	7	0.0125	76629 *s*	3	0.0125
65817	6	0.0125	77360	4	0.005
66217	7	0.0125	77483 *s*	4	0.005
66833	5	0.0125	77646 *s*	0	0.005

DESCRIPTION OF THE BANDS

A complete classification of bands in electron states and the assignment of vibrational transitions to each state could not be made on the basis of the available data. However the lack of sufficient data is not considered to be due to limitations in the experimental procedures. The resolution was probably much greater than necessary, and the accuracy in measurement adequate. The scarcity of data is due rather to the strong continuous absorption of acetone in this region, which occurs at the pressures necessary to bring out the weak bands, and thus prevents their observation. A more complete interpretation of the data may, however, occur to others, and for this reason it seems worth while to give a brief description of the bands.

At the end of the state with origin 51,171, previously described, there is a transmission extending to 60,086. The bands between 60,086 and 63,847 are all weak, those at the high frequency end being stronger. Relatively little continuous absorption is present in this region. Then a narrow transmission region extends to 65,213. At this point the strongest absorption region in the entire spectrum begins and extends to 67,000. Five bands are in this region. Another transmission region extends from 67,000 to 69,300. After this the continuous absorption seems to become stronger, although at the lowest pressures the strong bands can be easily observed. Beyond 78,000, however, the continuous absorption becomes so strong that no bands could be observed at the pressures used.

Bands in the first region show differences which are thought to be modifications of the fundamental frequencies 376 and 1066. Both frequencies are lowered but not more than in the 51,171 state. It is possible that two electron states are present in this region with origins 60,086 and 62,201.

The band at 65,213 is the strongest in the whole region, being clearly developed at less than 0.0025 mm pressure. This is considered as the origin of another electron state, which includes the four following bands. The same differences as above seem to be present and lowered to about the same extent.

It is difficult to be sure of the meaning of differences in the third region beginning at 69,316. There is a possibility that the fundamental frequencies are lowered so greatly in the high energy states that they cannot be recognized.

Originally it was thought that three Rydberg series were present in these bands and that the 51,171 state fitted into a series. After a more careful study of intensities, it now appears necessary to eliminate two of these series, on the basis of irregularities in intensities within the series. The series presented contains the strongest band, 65,213, as its first member, the second most intense, 73,834, as the second, and one of moderate intensity as the third, 77,360. The other members, if they exist, would be lost in the continuous absorption. The series converges at 82,767 cm^{-1} (10.20 volts). The formula is

$$\tilde{\nu} = 82{,}767 - R/(n-0.495)^2 \quad (n = 3, 4, 5, \cdots).$$

After a thorough search no other series containing more than two members could be found in the bands in this region, which was convincing from the standpoint of intensities.

Chemical Identification of the Radioelements Produced from Carbon and Boron by Deuteron Bombardment

DON M. YOST, L. N. RIDENOUR AND K. SHINOHARA, *Kellogg Radiation Laboratory and Gates Chemical Laboratory, California Institute of Technology*

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Chemical experiments were made on the radioactive substances resulting from the bombardment of carbon and boron by deuterons. Carbon is shown to yield an isotope of nitrogen and boron an isotope of carbon. The nitrogen so formed has a half-life of 10.5 minutes while that found by Curie and Joliot on bombardment of boron with alpha-particles has a half-life of 14 minutes. These facts are discussed.

INTRODUCTION

CURIE and Joliot[1] found that a radioactive element was produced on bombardment of boron with alpha-particles. They proposed the following nuclear reaction

$$_5B^{10}+{}_2He^4\rightarrow{}_7N^{13}+{}_0n^1,$$

the unstable isotope N^{13} disintegrating with the emission of a positron to become C^{13}. They were able to show chemically[2] that the active substance behaves like an isotope of nitrogen. The observed half-life of the activity was 14 minutes, and this has been independently confirmed by Ellis and Henderson.[3] Curie and Joliot suggested that the same radioelement could be obtained by bombarding carbon with high energy deuterons.

Various investigators[4] have found that the product of deuteron bombardment of carbon does exhibit radioactivity, but all are in agreement that the half-life is around 10.5 minutes. Since the nuclear reaction in this case seems very likely to be

$$_6C^{12}+{}_1H^2\rightarrow{}_7N^{13}+{}_0n^1,$$

inasmuch as observations on the recoil nuclei indicate that a particle of about the mass of the neutron is emitted in the creation of the radioactive nucleus,[5] the striking difference in half-life raises the question of the chemical nature of the element formed in this case. The three possibilities which exist are (a) that the radioelement formed from carbon by deuteron bombardment is not an isotope of nitrogen, but of some other element, (b) that it is a different nitrogen isotope from that formed from boron by alpha-particles, and (c) that the two radioelements are isotopic isobars; that is, both are N^{13}, but of different structure and therefore of different disintegration probability.

While the present work was in progress, the ingenious independent experiment of Cockcroft was reported,[5] showing that the active gas obtained from carbon after deuteron bombardment had about the same vapor pressures as liquid nitrogen. This eliminates a number of elements, but does not eliminate C or O if present as CO.

Radioactivity has also been observed by Crane and Lauritsen[4] after bombardment of boron by fast deuterons, and it seemed of interest to determine the nature of the radioelement in this case. It was known[6] that while all the activity cannot be driven off a graphite target even by heating to a bright red heat, the activity produced in a target of fused boric oxide can be completely removed as a gas condensible at liquid air temperatures by heating the target to about 200°. The former fact is not inconsistent with the idea that the active substance is nitrogen, which is known to be strongly adsorbed on carbon; the latter is taken to indicate that the radioelement from boron is C^{11}, formed in accordance with the reaction

$$_5B^{10}+{}_1H^2\rightarrow{}_6C^{11}+{}_0n^1\rightarrow{}_5B^{11}+{}_0n^1+e^+,$$

and present in the target as CO or CO_2.

[1] I. Curie and F. Joliot, Comptes rendus **198**, 254 (1934).
[2] I. Curie and F. Joliot, J. de phys. et rad. **5** [7], 153 (1934).
[3] Ellis and Henderson, Proc. Roy. Soc. **A146**, 206 (1934).
[4] Crane and Lauritsen, Phys. Rev. **45**, 430 (1934); Henderson, Livingston and Lawrence, Phys. Rev. **45**, 428 (1934); Hafstad and Tuve, Phys. Rev. **45**, 902 (1934); Cockcroft, Int. Conf. on Physics, London, 1934.
[5] Cockcroft, reference 4.
[6] Crane and Lauritsen, Phys. Rev. **45**, 497 (1934).

Experimental Method

Carbon was bombarded in the form of graphite and boron in the form of fused boric oxide by 0.8 and 0.9 mev. deuterons accelerated in the tube developed by Crane and Lauritsen for nuclear investigations.[7] Currents of about 40 microamperes were usually employed. The presence, amount, and half-life of the radioactive material were determined by quartz-fiber electroscopes constructed and kindly loaned by Professor Lauritsen, or by means of a Geiger counter whose cylindrical electrode was of aluminum about 0.2 mm thick.

The chemical identification was based on the well-known fact that isotopes are not appreciably separated by ordinary chemical reactions. Thus if an element consists of the fraction α of isotope a and $(1-\alpha)$ of isotope b, and if the fraction β of the total enters into a reaction, then $\beta\alpha$ and $\beta(1-\alpha)$ will be the fractions of each isotope that will have reacted. With the elements of large atomic weights this statement is almost exact, and in the case of hydrogen it is sufficiently true for the present purpose.

The experiments were always conducted on a gaseous form of the radioelement; in the case of boron this was prepared simply by heating the boric oxide target to about 600° in a closed vessel and washing the resulting gases into a gasometer with air. In the case of carbon, a thin layer containing practically all the activity was scraped off the upper surface of the target and burned with about 200 cc of air in a platinum boat in a quartz combustion tube. Air for the combustion was supplied from a specially constructed gas pipette. Small amounts of other gases could be added to the air used to burn the carbon or to the gases present in the gasometer in the experiments on boron. The following experiments were carried out; when any gas other than air was present, the fact is so stated.

Carbon bombarded by deuterons

The gases from the combustion of the carbon were passed first over heated copper oxide in all cases. They were subsequently passed through a train of solid or liquid absorbents, or they were collected over concentrated sulfuric acid in a second gas pipette similar to the first.

(1) The exit gas was passed through a train consisting of solid KOH (or soda lime), potash bulbs filled with 50 percent KOH, $CaCl_2$ and P_2O_5. The gas not absorbed was active. The solid KOH and $CaCl_2$ showed no activity. This experiment eliminates H, Li, Be, B and C as the active substances. The hydrogen would have been burned to H_2O and this would have mixed with the water of the KOH solution. The small amount of water vapor from the KOH solution would have been absorbed by $CaCl_2$ or P_2O_5. The oxides of Li, Be and B are not volatile at room temperatures. The hydrides of boron are burned by heated air and decomposed by alkali with the formation of B_2O_3 or its salts.[8] Carbon was present as CO_2 and this is readily absorbed by the alkalis present in the train.

(2) The exit gases were passed through alkaline pyrogallol and then collected in the pipette. The resulting gas was active. This result eliminates oxygen as O_2, since it is absorbed by the alkaline pyrogallol. If the oxygen were present as NO_2, it would undergo complete absorption in the potash.

(3) The gases resulting from the combustion of the graphite by a helium-air mixture were collected over concentrated sulfuric acid in the pipette. By passing the gas repeatedly (10 to 15 times) through alkaline pyrogallol it was freed from O_2 and CO_2. The gas so treated was strongly radioactive. It was next passed into an evacuated tube containing metallic calcium shavings and the calcium was then heated with a Bunsen burner. Extensive absorption of the gases took place. The tube was again evacuated to remove the helium and any other gases not absorbed by the calcium. After the contents of the tube had cooled and air had been admitted, the solid contents were removed and ground to a powder in a mortar. The powder showed strong activity. This result eliminates helium as the source of the activity, since it would be removed with the ordinary helium when the tube was evacuated.

The powder was then placed in a glass tube

[7] Crane, Lauritsen and Soltan, Phys. Rev. **45**, 507 (1934).

[8] Stock, *Hydrides of Boron and Silicon*, Cornell Univ. Press, Ithaca, N. Y. 1933, p. 54, 63.

equipped with a dropping funnel containing water. The gases evolved on adding water were radioactive. This result eliminates oxygen (if originally present as NO) and fluorine if present as the very unreactive CF_4 or C_2F_6. The oxygen would not be liberated as a gaseous substance in this procedure. If the fluorides of carbon were originally present, they would have been pumped out if they had not reacted with calcium, and they would have been converted to calcium fluoride and carbide had they so reacted; the calcium fluoride does not yield a volatile product in the alkaline solution such as existed on addition of water to the powder. Nitrogen would have been absorbed as Ca_3N_2, and this substance, on treatment with water, yields ammonia.

The combined results of the chemical experiments eliminate not only all the elements of the first row of the periodic system except nitrogen as the source of the radioactivity, but also all others. On physical grounds it is possible to state that the activity must be due to one of the elements H, He, Li, Be, B, C or N (unless the possibility of the emission of an electron from the carbon nucleus during bombardment is admitted, in which case O must be a possibility; no example of such a reaction has been established), since the total nuclear charge entering into the reaction producing the radioactive substance is 7. The total mass entering into the reaction is probably 14 and possibly 15 (although the abundance of C^{13} is very small), and we may certainly presume from the experiments on recoil radioactive nuclei[5] that the mass number of the radioactive product is surely not larger than 14 and is probably 13. Inasmuch as the only particles emitted from carbon under deuteron bombardment in observable numbers are known to be neutrons and protons, the radioactivity is probably due to C or N. Since we may assume in analogy with all cases of artificial radioactivity that the active substance is an isotope of mass number different from those known by mass spectra, it is likely to be C^{14} or N^{13}, and the latter is the more probable on the ground of the rarity of C^{13}, as well as from the fact that it emits positrons. The present experiment seems definitely to have established that it is nitrogen, and we may then infer that it is likely to be N^{13}.

Measurements on the half-life of the active gas at various stages in the chemical treatment yielded concordant values around 10.5 minutes, indicating that the activity is due to a single substance.

Boron bombarded by deuterons

The total mass entering into this reaction may be 12 or 13, corresponding to B^{10} or B^{11}. The total charge is 6, and we may again for safety admit the possibility of the emission of a negative electron from the nucleus. On physical grounds, the activity may, then, be due to H, He, Li, Be, B, C or N. Since a heavy particle must be emitted in the creation of the radioelement,[5] the total mass of the product must be 12 or smaller. The chemical experiments were as follows:

(1) A small amount of carbon dioxide was added to a sample of gas collected in the gasometer. One-half of the gas was tested and found to be active. The other half was passed repeatedly through KOH solution, and the resulting gas showed an activity of about one-third that of the first half, after correcting for known decay which took place while the operation was carried out. Some of the active materials evidently had been absorbed by the potash. Since Li and Be compounds are involatile these elements are eliminated as possible sources of all the activity.

(2) To a 150 cc sample of gas in the gasometer about 10 cc of carbon monoxide were added, and the mixture was then passed over heated cupric oxide. Half of the resulting gas was tested with an electroscope and found to be active. The other half was passed several times through 50 percent KOH solution and then into the electroscope. The resulting gas was inactive. These two results eliminate B, N_2 and O_2 as possibilities, since the volatile hydrides of B would burn to B_2O_3 on the hot CuO or be decomposed by the alkali,[8] and N_2 and O_2 would not be absorbed by KOH.

(3) Experiment 2 was repeated after 10 cc of helium had been added to the gas sample in the gasometer. The activity was absorbed by KOH. This result excludes He as the source of the activity since it is not absorbed by alkalies.

(4) A sample of gas to which CO and NO_2 had been added was passed over hot CuO and through a strong solution of $KMnO_4$ in 3 *N* sulfuric acid.

The resulting gas was active. The experiment was repeated but without passing over hot CuO. The result was the same. These results excluded H_2, and N as NO or NO_2, for hydrogen would burn to water and be mixed with the water in the permanganate solution; NO or NO_2 would be oxidized completely to HNO_3 by the acidified permanganate.[9] Fluorine, if present as BF_3, would be completely hydrolyzed and absorbed by the aqueous solution. Boron, if present as volatile hydrides, would be oxidized and decomposed by the heated CuO or hydrolyzed by the solution.

The results of the chemical experiments eliminate all elements in the first row of the periodic system except carbon. The gas driven from the boric oxide target has the properties of a mixture of carbon dioxide and carbon monoxide. Just why the newly formed carbon atoms should be oxidized partly to monoxide and partly to dioxide is not evident. It was not determined whether the two compounds were always formed in the same proportions.

Measurements on the half-life of the radioactive gas both before and after chemical treatment yielded the value 20.5 minutes in all cases, indicating that the activity is due to a single substance. Since C^{12} is stable, on the physical grounds outlined above, this substance is probably C^{11}.

We wish to express here our thanks to the Seeley W. Mudd fund for the financial support which made this work possible.

[9] Klemenc and Bunzl, Zeits. f. anorg. Chemie **122**, 315 (1922).

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Energy Levels of a Symmetrical Double Minima Problem with Applications to the NH_3 and ND_3 Molecules[1]

MILLARD F. MANNING, *Department of Physics, Massachusetts Institute of Technology*

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The energy levels for a potential energy $V=-C\,\mathrm{sech}^2 r/2\rho+D\,\mathrm{sech}^4 r/2\rho$ have been obtained by numerical solution of continued fractions. Values of the constants have been found such that the computed energy levels agree satisfactorily with the experimental values for the NH_3 and ND_3 molecules. The height of the ammonia pyramid is found to be 0.37A, the height of the potential hill is found to be 2076 cm^{-1}, and the dissociation energy is about five volts.

IT has been found possible to obtain a satisfactory interpretation of the infrared spectrum of ammonia by assuming that the molecule is shaped like a symmetrical pyramid. The potential energy as a function of the distance of the nitrogen atom from the plane of the hydrogens has the general shape indicated in Fig. 1. Whenever there are symmetrical double minima in the potential energy, the energy levels below the top of the center of the hill will be double, and above the top of the hill the levels for which the wave functions are symmetric will be shifted upward with respect to the levels for which the wave functions are antisymmetric.

Quantitative calculations of the behavior of the energy levels of a symmetrical double minima problem have been carried out by several authors.[2] The assumed forms of potential energy have been somewhat artificial, and except for the paper of Morse and Stueckelberg the methods used have been approximate. For these

[1] A preliminary report of these results is given in an abstract, Phys. Rev. **46**, 335 (1934).

[2] Morse and Stueckelberg, Helv. Phys. Acta **4**, 337 (1931); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); Rosen and Morse, Phys. Rev. **42**, 210 (1932).

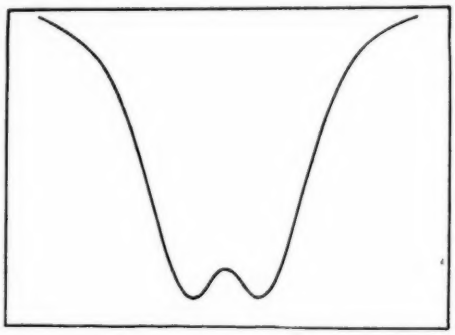

FIG. 1. Approximate form of the potential energy of the ammonia molecule as a function of the distance from the nitrogen atom to the plane of the hydrogen atoms.

reasons and because there are now available further data on the spectra of the NH_3 and ND_3 molecules further study of the problem has been considered worth while.

An expression for the potential energy which has the correct general characteristics and which permits an exact solution of the Schroedinger equation is:

$$V=\frac{1}{k\rho^2}\left[-\frac{\beta}{2}\left(\frac{\beta}{2}+\frac{1}{2}\right)\operatorname{sech}^2\frac{r}{2\rho}-D\left(\operatorname{sech}^2\frac{r}{2\rho}-\operatorname{sech}^4\frac{r}{2\rho}\right)\right], \quad (1)$$

where k equals $8\pi^2c/h$ times the reduced mass of the molecule for the type of vibration considered; r is the distance from the nitrogen atom to the plane of the hydrogens; and ρ, β and D are arbitrary constants.

The potential energy is:

$$-\frac{1}{k\rho^2}\frac{\beta}{2}\left(\frac{\beta}{2}+\frac{1}{2}\right) \quad (2)$$

at $r=0$, and zero at $r=\pm\infty$. There is a minimum at $\pm r_0$, where

$$\operatorname{sech}^2\frac{r_0}{2\rho}=\frac{(\beta/2)(\beta/2+\frac{1}{2})+D}{2D}. \quad (3)$$

The height of the central hill above the minima is

$$\frac{1}{k\rho^2}\frac{[D-(\beta/2)(\beta/2+\frac{1}{2})]^2}{4D}. \quad (4)$$

The Schroedinger equation for the vibration is:[3]

$$\frac{d^2R}{dr^2}+k\left[E+\frac{(\beta/2)(\beta/2+\frac{1}{2})+D}{k\rho^2}\operatorname{sech}^2\frac{r}{2\rho}-\frac{D}{k\rho^2}\operatorname{sech}^4\frac{r}{2\rho}\right]R=0, \quad (5)$$

where E is the energy in cm^{-1}.

Making the substitutions $x=\tanh^2(r/2\rho)$ and $R=(1-x)^{\beta/2-\lambda}F$, it is found that F must satisfy the differential equation:

$$(x-x)^2F''+[\tfrac{1}{2}-(\beta-2\lambda+\tfrac{3}{2})x]F'+[\lambda(\beta-\lambda-\tfrac{1}{2})+Dx]F=0, \quad (6)$$

where $$E=-(1/k\rho^2)(\beta/2-\lambda)^2. \quad (7)$$

If $F=\Sigma a_n x^{m+n}$, the recursion relation between successive coefficients is:

$$(m+n)(m+n+\tfrac{1}{2})a_{n+1}-(m+n-\lambda)(m+n+\beta+\tfrac{1}{2}-\lambda)a_n+Da_{n-1}=0. \quad (8)$$

The roots of the indicial equation are $m=0$ and $m=\frac{1}{2}$. The first corresponds to solutions which are symmetric about the plane of the hydrogens and the second to solutions which are antisymmetric. When $\beta/2-\lambda$ is positive, the boundary conditions are satisfied if there are no terms containing negative powers of x, and if the series converges at $x=1$. The values of λ for which these two conditions are fulfilled are the roots of the continued fraction

$$0=1-\cfrac{Q_0}{1-\cfrac{Q_1}{1-\cfrac{Q_2}{1-\cdots}}}, \quad (9)$$

where $$Q_n=\frac{(m+n+1)(m+n+\frac{1}{2})}{P_nP_{n+1}}D$$

$$P_n=(m+n-\lambda)(m+n+\beta+\tfrac{1}{2}-\lambda). \quad (10)$$

As n is increased Q_n becomes smaller and after some reasonable number of terms can be neglected in comparison with unity. For given values

[3] See Rosen and Morse for a justification of the method of normal coordinates as applied to polyatomic molecules.

of β and D, the values of λ for which Eq. (9) is satisfied can be found numerically by a process of successive approximations. By this method it was found that $\beta=70$, $D=1920$, $k\rho^2=2.885\times10^{-2}$, give energy levels which are in good agreement with those found experimentally for the parallel type vibrations of ammonia. The results are given in Table I.

TABLE I.

	NH_3		ND_3	
	calc.	obs.	calc.	obs.
0_s	0	0	0	0
0_a	0.83	0.67	<0.2	
1_s	935	932± 0.5	746.0	746± 2
1_a	961	964± 0.5	748.5	755±10
2_s	1610	1600±15	1379	1363± 2
2_a	1870	1910±15	1434	1437±10
3_s	2360	2380±15	1852	1831± 2
3_a	2840		2140	

In order to find r_0 from Eq. (3) and the value of $k\rho^2$ it is necessary to know the reduced mass for the vibrations considered. The reduced mass cannot be found unless some further assumptions about the motion are made. If the binding between hydrogen and hydrogen is much stronger than the binding between nitrogen and hydrogen, the hydrogens will move as a rigid triangle, the reduced mass will be independent of amplitude, and k will be equal to 1.47×10^{15}. If, as is probably true, the binding between hydrogen and nitrogen is much stronger than the binding between hydrogen and hydrogen, the motion will consist of a bending of the nitrogen–hydrogen bond. For this sort of motion the reduced mass for finite amplitudes of vibration can be determined only as an average and will depend upon the amplitude of vibration. For given dimensions of the pyramid, the reduced mass for infinitesimal vibrations can be calculated and k is equal to 1.66×10^{15}. Even for finite amplitudes of oscillation this value is probably a good approximation. These two values of k are probably upper and lower limits. The corresponding values of the height of the pyramid are 0.40A and 0.37A.

In accordance with the general theory of isotope effects, the force constants should be the same for the ND_3 molecule as for the NH_3 molecule. For the ND_3 molecule the constants $(\beta/2)(\beta/2+1/2)$ and D should be increased by the same ratio as the reduced mass is increased. It turns out that this ratio is practically the same whichever assumption is made about the reduced mass for the NH_3 molecule. The constants used for the ND_3 molecule were $\beta=91.40$, $D=3261$, $k\rho^2=4.899\times10^{-2}$. The energy levels are given in Table I.

The lowest four levels of NH_3 are from data given by Wright and Randall.[4] The rest of the data were very kindly supplied by Dr. W. S. Benedict in a private communication.

The agreement is as good as can be expected considering the approximations that have been made, and considering that only three constants were used to fit eleven experimental values. A better estimate of the form of the potential curve can be made when accurate data on the separation of the doublets of the ND_3 spectrum are available.

The author wishes to express his appreciation to Professor P. M. Morse for many helpful suggestions.

[4] Wright and Randall, Phys. Rev. **44**, 391 (1933).

Active Hydrogen

A. C. GRUBB AND A. B. VAN CLEAVE,[1] *University of Saskatchewan*

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Dry hydrogen can be activated in an electric discharge if the pressure and voltage are carefully regulated. Active hydrogen reduces metallic sulphides whose heat of formation is 22,000 cal. or less. The active gas is decomposed by 3 cm of well packed glass wool. A quantitative method is given for the determination of active hydrogen. Less of the active gas is formed in a tube coated with stearic acid or phosphoric acid than when no coating is employed. The decay reaction was found to follow the expression for a unimolecular reaction. The rate of decay appears to be independent of the wall surface. The period of half-life at room temperature and 40 mm pressure is 0.2 sec. approximately. The energy of formation of active hydrogen is approximately 18,000 cal. The energy of activation for the decay of the active constituent is approximately 17,800 cal. The properties of active hydrogen are considered in relation to the properties predicted for H_3.

SINCE the pioneer work of Sir J. J. Thomson[2] who showed by positive ray analysis that the group H_3^+ existed, and the investigations of I. Langmuir[3] and R. W. Wood[4] who found that a special chemical activity shown by hydrogen was due to atoms, many investigators[5–13] have studied the properties of active hydrogen. During the early work, the idea prevailed that neutral H_3 could be formed in discharge tubes of different design from the Wood's tube which produced atomic hydrogen from wet gas. Attempts to confirm some of the work on triatomic hydrogen led investigators[14] to consider that the contamination of the discharge tube had influenced the positive results. Up to this time no concise information had been given in regard to the exact quantitative conditions under which triatomic hydrogen could be formed. No quantitative method had been developed so that consistent results could be obtained for consecutive determinations as had been accomplished for ozone.

Through their investigations, mathematical physicists had concluded that any triatomic hydrogen formed in discharge tubes by the collision of an atom with a molecule of hydrogen could exist for only a very short time. The life of H_3 was estimated to be of the order of 10^{-8} seconds.[15] This time was too short for triatomic hydrogen to leave the discharge and manifest the properties claimed for it. This led many workers to consider that the only activity manifested by hydrogen was due to atoms.

The first consistent quantitative work reported for active hydrogen formed under conditions not favorable to the production of hydrogen atoms is that of Binder, Filby and Grubb.[16]

The present study is largely the presentation of new evidence for the existence of an active form of hydrogen which differs markedly in its properties from atomic hydrogen.

EXPERIMENTAL METHOD

Apparatus

The arrangement of apparatus is shown in Fig. 1. A high pressure tank of electrolytic gas was used as a source of hydrogen. The gas was purified by passing it through a strong solution of sodium hydroxide, a soda lime tower, an electric

[1] This communication is based on a thesis submitted by A. B. Van Cleave in 1933 in partial fulfilment of requirements for the degree of Master of Science in Chemistry at the University of Saskatchewan, Saskatoon, Canada. Mr. Van Cleave was the holder of a Bursary under the National Research Council of Canada.

[2] Sir J. J. Thomson, Proc. Roy. Soc. **A89**, 20 (1911).

[3] I. Langmuir, J. Am. Chem. Soc. **34**, 1310 (1912).

[4] R. W. Wood, Phil. Mag. **42**, 729 (1921).

[5] Wm. Duane and G. L. Wendt, Phys. Rev. **7**, 689 (1916).

[6] Y. Venkataramaih, Nature **106**, 46 (1920).

[7] G. L. Wendt and R. S. Landauer, J. Am. Chem. Soc. **42**, 930 (1920); **44**, 510 (1922).

[8] P. Anderson, J. Chem. Soc. **121**, 1153 (1922).

[9] A. E. Mitchell and A. L. Marshall, J. Chem. Soc. **123**, 2448 (1923).

[10] K. F. Bonhoeffer, Zeits. f. physik. Chemie **113**, 199 (1924).

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[12] M. Scanavy-Grigoriewa, Zeits. f. anorg. allgem. Chemie **159**, 55 (1926).

[13] F. Paneth, E. Klever and K. Peters, Zeits. f. Elektrochemie **33**, 102 (1927).

[14] H. M. Smallwood and H. C. Urey, J. Am. Chem. Soc. **50**, 620 (1928).

[15] Conrad, Zeits. f. Physik **75**, 504 (1932).

[16] Binder, Filby and Grubb, Can. J. Research **4**, 330 (1931).

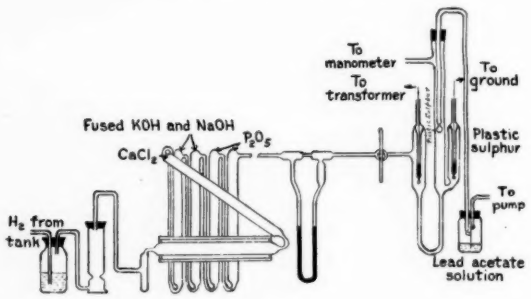

FIG. 1.

furnace containing platinized asbestos heated to 550°C, two towers containing fused potassium and sodium hydroxide and finally two towers of phosphorus pentoxide. The rate of flow of hydrogen was measured by a calibrated flowmeter of the type used by Benton.[17] A fine capillary tube and a stopcock were placed between the flowmeter and discharge tube to facilitate in the adjustment of pressure which was maintained by a Cenco Hyvac pump and measured by an open mercury manometer.

The vacuum discharge tube was made from ordinary glass tubing 6 mm inside diameter and shaped in the form of a U-tube to permit immersion in an ice-water bath or freezing mixture. Two 14 mm tubes were sealed to the ends of the U-tube. Electrodes of No. 15 (B. and S.) platinum wire were sealed into 6 mm tubes which were connected to the 14 mm tubes by inner seals as shown in Fig. 1. The distance between the electrodes varied from 20 to 30 cm. The reagent on which the action of the active hydrogen was tested was placed at any desired distance from the discharge in the wide reaction chamber on the ground electrode side. Unless otherwise stated, the inner surface of all tubes was coated with stearic acid. All results reported were taken with the tube immersed in an ice-water bath.

The electrical energy was obtained from a rotary converter which supplied an alternating current through a water rheostat to the primary of a Thordarson 25,000 volts, 1 kva, type R transformer. The primary wattage, voltage and amperage were measured with standard Weston instruments.

[17] Benton, J. Ind. and Eng. Chem. **11**, 623 (1919).

1. Blanks and tests for atomic hydrogen

In a previous investigation[16] it was found that plastic sulphur could be used as a testing agent for active hydrogen without contaminating the discharge with sulphur blown back into the discharge tube. But to eliminate all sources of contamination careful blanks were run. In this work a perfect blank consisted in running the hydrogen from the purifying system through the tube with the discharge off and over plastic sulphur, for two hours at 3 liters per hour without producing a trace of lead sulphide, as shown by a blank test paper. The plastic sulphur was then removed from the reaction chamber, the discharge turned on and the gas under the same conditions directed against lead acetate paper producing no lead sulphide.

The first part of the blank showed that the gas was free from hydrogen sulphide, that it contained no constituent which reacted with sulphur, and that the sulphur contained no volatile sulphides. The second part of the blank showed that the hydrogen contained no sulphur compound capable of forming hydrogen sulphide in the discharge, that the tube was free from contaminations, and that the escaping gas contained no silicon hydride as advocated by Hiedemann.[18] These tests were tried repeatedly all through the course of this work and in no case was any evidence for silicon hydride found.

Some authors considered that our former results were due to atomic hydrogen. Very extensive tests were made for atomic hydrogen. A fragment of tungsten wire was mounted in place of the plastic sulphur and placed 3, 2, 1 cm, respectively, from the discharge and finally into the discharge. For each of the positions for the tungsten, the pressure was varied from 40 mm down to 0.5 mm and as viewed in the dark there was no trace of a glow on the tungsten. At 0.5 mm pressure and with the wire in the discharge, had atoms been present, the tungsten should have been incandescent. These results confirm those of R. W. Wood,[19] who found that dry hydrogen from a discharge brought in contact with a small tungsten wire produced no glow.

[18] E. Hiedemann, Zeits. f. physik. Chemie **A153**, 210 (1931).

[19] R. W. Wood, Phil. Mag. **44**, 538 (1922).

2. The critical potential-pressure relation for activity

During an attempt to substitute a 20,000 volt Thordarson transformer for the 25,000 volt instrument that had been used, it was observed that the two transformers operated at the same primary wattage did not produce the same results. No sulphide was produced when the lower voltage instrument was used. Further investigation showed that the energy input of this instrument had to be increased considerably to give positive results. With a pressure of 40 mm in the tube and the plastic sulphur 20 cm from the discharge, the original transformer, using 90 volts in the primary, produced a discharge that gave good sulphide tests. These results could not be duplicated with the lower voltage instrument operated with 110 volts in the primary.

The primary potential-pressure relation for two tubes, using the 25,000 volt transformer, is shown in Fig. 2. Tube No. 1 was constructed with reaction chamber 12 mm in diameter and with 22 cm between electrodes while tube No. 2 had a reaction chamber 16 mm in diameter and electrodes 26 cm apart. In obtaining the data represented by points on these curves, first a run was made below the critical voltage and then the primary voltage raised in subsequent runs in steps of $2\frac{1}{2}$ volts until at the end of a half hour run only a faint trace of sulphide appeared on the test paper. If the potential is raised a few volts above the minimum value for any pressure, the amount of sulphide formed is greatly increased. Perfect blanks may be obtained at will by lowering the potential a few volts below the minimum. Preliminary experiments showed that tube No. 1 could be operated with plastic sulphur mounted 20 cm from the discharge except in the pressure range 70 to 80 mm. No sulphide was obtained in this region at any voltage up to 110.

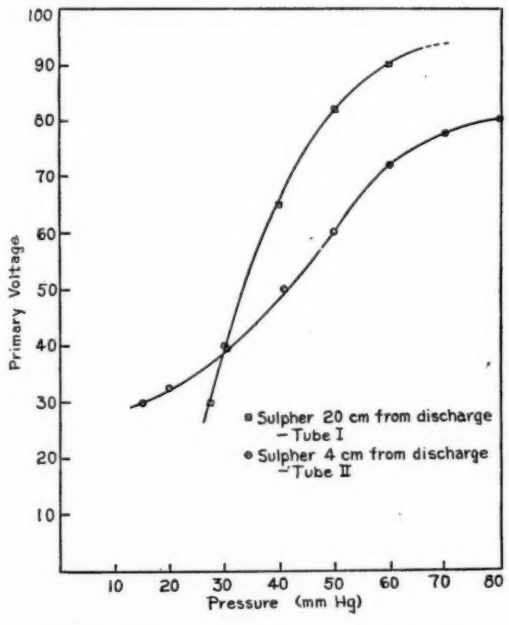

FIG. 2. Variation of critical voltage with pressure.

3. Reduction of sulphides

Bonhoeffer[10] studied the energy associated with atomic hydrogen by using it to reduce various compounds including sulphides. In our investigation pure sulphides were prepared by standard methods[20] and mounted 4 cm from the discharge in tube No. 2. Careful blank runs were made just before the sulphide was introduced into the reaction chamber and also after it was removed. Both silver sulphide and cuprous sulphides were very greatly reduced during a half hour run while thallous sulphide showed only a slight reduction. Nickel sulphide was reduced slightly 1 cm from the discharge but iron sulphide was not reduced.

TABLE I. *Reaction of sulphides to active hydrogen.*

Sulphide	Heat of formation Int. Crit. Tab.	Reaction to active hydrogen
Ag_2S	5.02 kg cal.	Reduced (markedly)
Cu_2S	18.97 kg cal.	" "
NiS	20.78 kg cal.	Reduced slightly 1 cm from discharge
Tl_2S	21.98 kg cal.	Reduced (slightly)
FeS	23.06 kg cal.	Not reduced

4. Effect of glass wool upon the stability of active hydrogen

In some investigations the hydrogen from the discharge has been passed through glass wool before coming in contact with sulphur. The amount of wool used by different investigators has varied from 1 to 10 cm. In the present study

[20] Keyes and Felsing, J. Am. Chem. Soc. **42**, 246 (1920).

no glass wool was used except in this special test. The plastic sulphur was mounted 4.5 cm from the discharge in a special tube into which glass wool could be packed. A run, at 85 volts and 40 mm pressure, made for 30 min. without any glass wool present gave a good sulphide test. Runs at the same potential and pressure were then made using increasing quantities of glass wool between the discharge and the sulphur, but it required a column 2.5 cm in length weighing 0.2535 g to decompose completely the active hydrogen. The perfect blank tests also showed the tube was not contaminated with sulphur.

5. Quantitative estimate and the rate of decay of active hydrogen

Since molecular hydrogen has a small amount of reducing action upon potassium permanganate solution[16] the use of this reagent to absorb hydrogen sulphide quantitatively from excess hydrogen is not entirely satisfactory. It necessitates the use of carefully determined blanks.

Other methods were tried but the following procedure was found to be most satisfactory. The sulphide was absorbed in 25 cc of 0.5N sodium hydroxide solution. After the run the base was neutralized with standard sulphuric acid, the correct amount having been previously determined using methyl red as indicator. The hydrogen sulphide was titrated with N/400 iodine solution using starch as an indicator. It was found that 0.4 cc of the iodine solution was required with starch to give a visible color to the neutralized reagents. This blank was subtracted from each titration. The results obtained by this method were quite consistent. The following is an example of the results for runs made under duplicate conditions. The values were 2.85 cc, 2.75 cc, 3.00 cc, 2.85 cc of N/400 iodine solution. The behavior of tubes in respect to the distance the sulphur was located from the discharge in the study of the critical voltage-pressure relation and the destruction of the activity by glass wool seemed to indicate that the active hydrogen had a very rapid rate of decay. By maintaining a constant rate of flow, pressure and voltage with the sulphur testing agent located at varying distances from the discharge it was possible to obtain results that were an indication of the order of the decay reaction. If the rate of flow of hydrogen, the pressure, the diameter of the reaction tube in which the testing agent is mounted are known, then by the method of refills the time taken for the hydrogen to travel a definite distance may be calculated.

A new tube of similar design was constructed having a reaction chamber whose diameter was 14.6 mm. The walls of this tube were left uncoated since it was planned to make a study of the wall effect upon the formation and decay of the active constituent. For the initial determination the plastic sulphur was mounted 2 cm from the discharge. Subsequent determinations were made at distances of 3, 4, 5, 6, 7 and 8 cm from the discharge. Runs were made with the sulphur mounted at greater distances but the amount of sulphide formed was too small to be titrated by the quantitative method used. However, preliminary runs with lead acetate paper as a testing agent had shown a range of 15 cm for the active hydrogen. This result shows that an extremely small concentration of hydrogen sulphide may be detected by a lead acetate test paper. After completing the results for the tube uncoated, it was taken down and both discharge tube and reaction chamber coated with a thin layer of very pure stearic acid. The tube was then replaced and operated under identical conditions as before and results secured for the coated tube. The stearic acid was removed and the tube coated with syrupy phosphoric acid. Runs were again made under duplicate conditions although not so many points were obtained as before. The only variable factor in these data is the wall coating. The same tube was used throughout and the runs were made under

TABLE II. *Values obtained for the titration of sulphide formed by active hydrogen.*

Duration of runs—2 hr. Pressure—42 mm
Hydrogen flow—3 liters per hr. Primary e.m.f.—85 volts

Distance of plastic sulphur from discharge in cm	Cc. of N/400 iodine solution		
	Tube uncoated	Stearic acid coating	Phosphoric acid coating
2	5.70	4.45	—
3	3.90	—	—
4	2.85	1.95	1.85
5	1.85	—	—
6	1.10	.85	—
7	.45		.35
8	.00		

identical velocity, pressure and voltage conditions. The titration values are the average of several determinations as illustrated above. The results obtained for the tube operated under the conditions described above are given in Table II.

Calculations were made of the time required for the hydrogen to travel from the initial position of the sulphur to each subsequent position. The amount of iodine used in each titration is directly proportional to the concentration of active hydrogen. The logarithms of these titration values plotted against the time are shown in Fig. 3. The straight line indicates that the decay of active hydrogen is a reaction of the first order and appears to be unimolecular at the pressure studied.

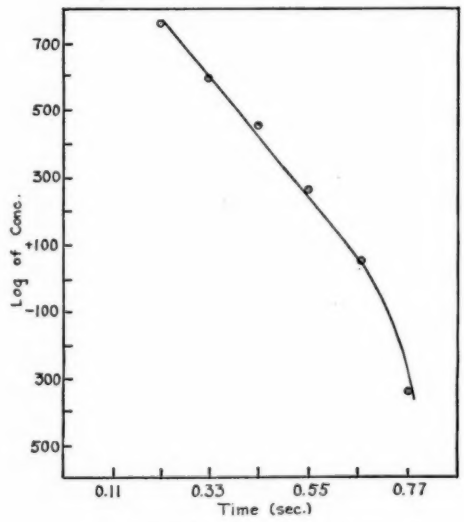

FIG. 3. Plot of log C against time.

Calculations

For a unimolecular reaction the specific reaction rate k is given by the equation

$$k=2.303/(t_2-t_1)\ \log\ a/(a-x).$$

As applied, a is the initial concentration of active hydrogen at time t_1 and $a-x$ is the concentration at time t_2. Since the amount of iodine used to titrate the hydrogen sulphide absorbed is proportional to the concentration of active hydrogen, these titration values have been substituted in the above expression to calculate the reaction rate constant k. The k values agree very well except the last value for the tube uncoated, and the k value for the tube coated with phosphoric acid. These decay constants represent the rate of decay over the last centimeter of the range where the concentration or partial pressure of the active hydrogen is extremely low. There is probably more error in the determination of this k value than in the preceding ones. However, Hirst and Rideal[21] found that the decay constant for nitrogen pentoxide tended to increase at very low pressures.

TABLE III. *Specific decomposition rate of active hydrogen for different tubes calculated from data in Table II.* Temp. 298T. Values of k (sec.$^{-1}$).

Glass walls	Stearic acid walls	Phosphoric acid walls
3.4	—	—
3.2	—	—
3.4	3.7	—
3.7	3.7	—
4.6	—	5.0

The decay reaction for active hydrogen appears to occur independently of the surface of the container and may be considered as a homogeneous gas reaction of the first order.

DISCUSSION OF RESULTS

The evidence presented in the experimental work just described shows that active hydrogen has properties not previously reported by other workers. The reports of former investigations have included but brief statements of the design of tubes and the types of electrical equipment used. Apparently it was not recognized that any special control of the electrical conditions needed to be considered if the results were to be consistent. Also in the design of the discharge tube, the distance between electrodes, the diameter of the reaction chamber and the distance of the plastic sulphur from the discharge are factors to be considered if the investigators' results are to be confirmed. No doubt many of the negative or sporadic results recorded in the literature may be due to the use of potentials that were below the minimum for the pressure or to the fact that the sulphur was mounted beyond the range for the active gas. Preliminary experiments showed

[21] Hirst and Rideal, Proc. Roy. Soc. **A109**, 526 (1925).

that with other conditions identical, the range of the active constituent varied inversely with the diameter of the reaction chamber. This would also indicate a negligible wall effect.

There are two energy relations to be considered on the basis of the data given—the energy of activation of the hydrogen in the discharge, and the energy of activation for the decay of the active constituent.

The amount of energy absorbed from the discharge by one mole of hydrogen in changing from the inactive to the active state is the energy of activation. In a collision between active hydrogen and a metallic sulphide which results in the reduction of the sulphide and the formation of hydrogen sulphide, the reaction may be indicated as follows:

$$(\text{active hydrogen})+\text{MS}=\text{H}_2\text{S}+\text{M}.$$

If the energy evolved in the formation of MS is 23,000 cal. and that evolved in the formation of H_2S is 5260 cal., then the amount of energy required to activate the hydrogen will be approximately 18,000 cal. There was a noticeable decrease in the amount of metallic sulphide reduced in testing various sulphides as the heat of formation for the sulphide increased. Thallium sulphide was only slightly reduced 4 cm from the discharge, nickel sulphide slightly reduced at 1 cm from the discharge, and iron sulphide was not reduced. Therefore it is concluded that the energy acquired by the hydrogen as it leaves the discharge is at least 18,000 cal.

In determining the energy of activation for the decay reaction, the usual method involves the determination of k's at two temperatures, and the calculation of E, using the integrated form of the Arrhenius equation:

$$\log k_2/k_1=-E(T_2-T_1)/2.303RT_2T_1. \quad (1)$$

The very high rate of decay for this reaction makes it extremely difficult to bring the system to temperature equilibrium for the determination of k at some other temperature. Therefore, a suggestion has been taken from the paper by H. Eyring and F. Daniels.[22]

They state, "The value of E can be calculated more accurately with the equation

$$k=se^{-E/RT}, \quad (2)$$

or

$$\log k=-E/2.303R\times 1/T+\log s, \quad (3)$$

from k at one temperature on the assumption that s is about 5×10^{13} than it can be calculated in the usual way from the k's at two temperatures in Eq. (1)." The accuracy of such a calculation depends upon the constancy of s. This relation has been discussed by several investigators[22, 23, 24] who consider that for unimolecular reactions, s may be considered a constant within certain limits. The rate constant for the decay reaction in the tube coated with phosphoric acid is 1.3 times greater than the average, yet the value for the energy of activation is but 200 cal. less than the average. The period of half-life at 25°C may be calculated by the equation: $t_{\frac{1}{2}}=0.6932/k$. If the average k for the decay reaction in the tube with glass walls is used, $t_{\frac{1}{2}}$ is equal to 0.188 sec. For the tube coated with stearic acid, $t_{\frac{1}{2}}$ is equal to 0.185 sec. If we use the average of the first four constants found for the glass tube, $t_{\frac{1}{2}}=0.20$ sec.

TABLE IV. *Calculated energy of activation for the decay reaction using the rate constants of Table III and* $s=5\times 10^{13}$.

Tube glass walls	Tube stearic acid walls	Tube phosphoric acid walls
17.8 kg cal.		
17.9 kg cal.		
17.8 kg cal.	17.8 kg cal.	
17.8 kg cal.	17.8 kg cal.	
17.7 kg cal.		17.6 kg cal.

The question of the identity of active hydrogen may be somewhat involved but the new experimental evidence presented tends to eliminate some ideas and to support others. Some investigators[25] consider that any activity manifest by hydrogen is due to atoms. A tube of the Wood's type, using moist hydrogen or coated with phosphoric acid, is usually employed for producing hydrogen atoms. The atoms will reduce metallic

[22] H. Eyring and F. Daniels, J. Am. Chem. Soc. **52**, 1482 (1930).

[23] Christiansen and Kramers, Zeits. f. physik. Chemie **104**, 451 (1923).

[24] C. N. Hinshelwood, Chemical Reviews **3**, 227 (1926).

[25] G. R. Schultz, J. Phys. Chem. **35**, 3186 (1931).

sulphides of much higher heat of formation than 23,000 cal. per mole since the energy available by their recombination is of the order of 100,000 cal. per mole.

The recombination of hydrogen atoms is considered to be a trimolecular gas reaction influenced by the walls of the vessel.[26, 27, 28]

The discharge tube used in this investigation is of different design and is operated under different conditions from that usually employed for the production of hydrogen atoms.

The same tube coated with stearic acid or phosphoric acid and operated under identical conditions produced one-third less active hydrogen than when used with glass walls. This is the opposite of what one would expect if atoms were present. However, this is in agreement with the work of H. G. Thode and A. C. Grubb[29] who found less ozone produced in a discharge tube whose walls were coated with stearic acid or paraffin than was produced in the same tube with the wall surface of glass.

The specific reaction rate constant for the decay of active hydrogen is practically constant under the conditions described, and the decay appears to be a homogeneous reaction. The logarithms of the concentration plotted against the time gives a straight line which is in agreement with the conditions for a unimolecular reaction.

All the evidence points to the formation and decay of a complex molecule. Unimolecular reactions are found chiefly among complex molecules.

Triatomic hydrogen, once accepted and later held in disrepute by mathematical physicists, is now granted a "sticky" existence by Eyring.[30, 31] These authors calculate the minimum energy of activation on the basis of the collision of three hydrogen atoms on a straight line. Their result for this type of a collision is 13 kg cal. A higher energy of activation is found for collisions not on a straight line. Experimentally one might expect the majority of collisions to be at an angle, and the statistically averaged energy of activation for the formation of H_3 to be greater than the minimum of 13 kg cal.

For the unimolecular decomposition of H_3 the minimum energy of activation predicted by Eyring is 1.6 kg cal. This quantity of energy as represented on the contours "is the depth of the potential energy basin measured from the bottom to the lowest point in the rim of the basin through which the ball can escape to the outside." This would limit the escape to a particular point on the rim for those molecules having just the minimum energy of activation. But for those molecules having an excess of E over the minimum the region of escape would cover a larger fraction of the rim. The statistically averaged value for the energy of activation would be higher than 1.6 kg cal. and lower than 24 kg cal. required for an H_3 molecule stable at room temperature. The value of 17.8 kg cal. for the energy of activation for the decomposition of active hydrogen is within the limits of Eyring's predicted result for H_3.

Sir J. J. Thomson[32] has shown that a fleeting neutral type of H_3 exists and that it can be obtained from normal hydrogen. He considers that the group is composed of three atoms of hydrogen of mass one. (Private communication.)

Since other complexes[33] possibly involving the isotope exist in a discharge through hydrogen, a disagreement between experimental and theoretical physics does not obviate the possibility that some other complex may be involved in the activity manifest in this study. However, H_3 would be the simplest complex to undergo unimolecular decomposition. It is trusted that future investigation will elucidate this point.

Thanks and appreciation are expressed to the National Research Council of Canada for financial assistance during the course of this investigation.

[26] H. Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929).
[27] Steiner and Wicke, Zeits. f. physik. Chemie, Bodenstein-Band, 817 (1931).
[28] H. Smallwood, J. Am. Chem. Soc. **56**, 1542 (1934).
[29] H. G. Thode and A. C. Grubb, Trans. Electrochem. Soc. **63**, 297 (1933).
[30] Henry Eyring, Chem. Rev. **10**, 111 (1932).
[31] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).
[32] Sir J. J. Thomson, Phil. Mag. **17**, 1025 (1934).
[33] P. Zeeman and J. De Gier, Proc. K. Akad. Wetensch Amsterdam **36**, 717 (1933).

Triatomic Ions in Mixtures of the Hydrogen Isotopes

OVERTON LUHR, *Physics Laboratory, Union College**

(Received January 4, 1935)

A mass spectrograph analysis has been made of aged ions in mixtures of hydrogen and deuterium. The concentration of deuterium was varied from 84 percent to less than one percent. After drifting through 5 cm of gas at about 0.5 mm pressure, the ions were found to be over 95 percent triatomic; that is, H_3^+, H_2D^+, HD_2^+ and D_3^+. Measurement of the relative intensities of the triatomic ion peaks indicates a slightly greater number of H_3^+ and D_3^+ ions compared to H_2D^+ and HD_2^+ than would be expected from probability considerations if the H and D atoms behaved exactly alike. This tendency for like atoms to group together may be accounted for by taking cognizance of the proper equilibrium constant for the different types of diatomic molecules in the gas mixtures employed. There is no evidence of further preferential grouping in the formation of the triatomic ions from the primary molecular ions. The relative heights of the triatomic ion peaks may be used to determine the abundance of the isotopes in a sample of gas.

INTRODUCTION

IF ions produced by a glow discharge in ordinary hydrogen at relatively high pressures are allowed to age by drifting at low speed through some cm of gas, it is found that the primary diatomic ions change over almost completely to triatomic ions of molecular weight three. The number of protons is comparatively small; so it is easily possible to attain a condition where 95 percent or more of all the ions present are triatomic. As would be expected, the same phenomenon occurs in mixtures of the hydrogen isotopes, only there the triatomic ions may have molecular weights of 3, 4, 5 and 6 depending on the combination of light and heavy hydrogen atoms which have formed a particular ion. These ions have been observed by several experimenters,[1, 2] and the triatomic ion, H_2D^+, of mass 4 has been employed by Luhr and Harris[3] to determine the concentration of deuterium in a sample of hydrogen where the percentage of deuterium is small. The purpose of this paper is to apply the method of Luhr and Harris to the general case for any concentrations of deuterium and protium. From measurement of the ratio of the intensities of the triatomic ion peaks it should be possible to determine the relative concentrations of the isotopes in the sample of gas and to find out something about the atomic processes involved in the formation of the triatomic ions.

APPARATUS AND METHOD

The sample of gas to be analyzed was prepared by the decomposition of water on a tungsten filament heated to about 1000°C. This method has been described by A. and L. Farkas and P. Harteck,[4] and furnishes a very convenient means of obtaining hydrogen from water where a small quantity is desired. For the samples containing the largest concentrations of deuterium a drop of heavy water (specific gravity, 1.1054; 95 percent deuterium or better) was pumped back and forth across the tungsten filament by condensing in liquid air traps until the water was nearly all decomposed. Despite all reasonable precautions the concentration of deuterium had dropped to about 84 percent by the time it was analyzed in the mass spectrograph. The gas was not pumped off after passing through the mass spectrograph but was circulated through the apparatus and was diluted as desired by the addition of tank hydrogen. This latter procedure was possibly undesirable as the various molecules in the gas may not have attained equilibrium. However, the results were the same when the diluted gas was prepared by decomposing a mixture of light and heavy water; so it seems likely that the glow discharge or the presence of catalysts such as nickel[5] in the system resulted in approximate equilibrium.

The mass spectrograph and discharge tube have been described previously.[6] A glow discharge

* Experimental work performed at Massachusetts Institute of Technology.

[1] K. T. Bainbridge, Phys. Rev. **42**, 1 (1932).

[2] W. Bleakney and A. J. Gould, Phys. Rev. **45**, 281 (1934).

[3] O. Luhr and L. Harris, Phys. Rev. **45**, 843 (1934).

[4] A. and L. Farkas and P. Harteck, Proc. Roy. Soc. **A144**, 467 (1934).

[5] Gould, Bleakney, Taylor, J. Chem. Phys. **2**, 362 (1934).

[6] O. Luhr, Phys. Rev. **44**, 459 (1933).

was maintained between water-cooled aluminum electrodes. Some of the ions passed through a grid and were aged by drifting through 5 cm of gas at about 0.5 mm pressure, under the action of a field of about a volt per cm. They then entered a Dempster-type mass spectrograph through a 0.01 mm slit, and the current to the collector was measured as a function of the magnetic field strength, the electric accelerating field being kept constant. The defining slits of the apparatus having been previously adjusted for work requiring high resolution, heights of the ion peaks were only approximately proportional to the intensity of the ion beams. No serious error was introduced, however, when the intensities were of the same order of magnitude. As would be expected, the smaller peaks were relatively too large when the ratio of the heights was of the order of a hundred, and in such cases more consistent results were obtained by the use of areas under the peaks.

Experimental Results

Figs. 1 to 4 show typical mass spectrograph curves for various concentrations of the isotopes. Fig. 1 shows results for the highest concentration of deuterium obtained—about 84 percent. Figs. 2 and 3 show results when the deuterium has been diluted by the addition of tank hydrogen. Fig. 4 is a typical result obtained when the sample of hydrogen was prepared by decomposition of water containing 0.60 percent deuterium. This water was obtained from the chemistry department of M. I. T.

Two effects should be noted here. First, it was found that when tank hydrogen was added to the sample, dilution did not occur in the expected ratio; that is, there was a tendency for the deuterium to remain when the excess gas was pumped off. This effect was probably due to the difference in diffusion rates. For example, the percentage of deuterium found in Fig. 3 should have been one-fourth that found in Fig. 2. Actually, it was slightly less than one-third. Second, there was a tendency for the concentration of deuterium to decrease with time as the gas containing high percentages of deuterium was circulated through the system. Likewise, it was difficult to rid the apparatus of deuterium once it had been used. This effect presumably resulted from adsorbed gas on the walls.

Discussion of Results

If it is assumed that the H and D atoms behave exactly alike in the formation of triatomic ions, straight probability gives the results shown

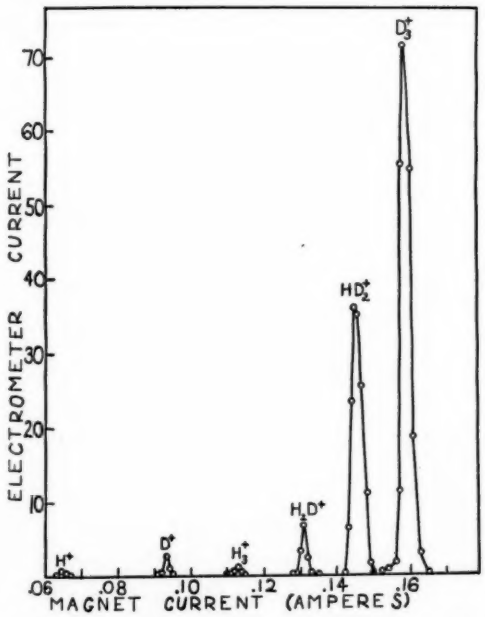

Fig. 1. Aged ions in a mixture of the hydrogen isotopes containing about 84 percent deuterium.

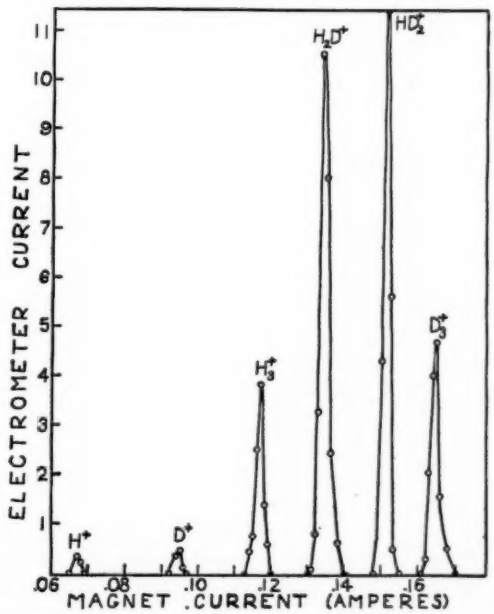

Fig. 2. Aged ions in a mixture containing nearly equal parts of hydrogen and deuterium.

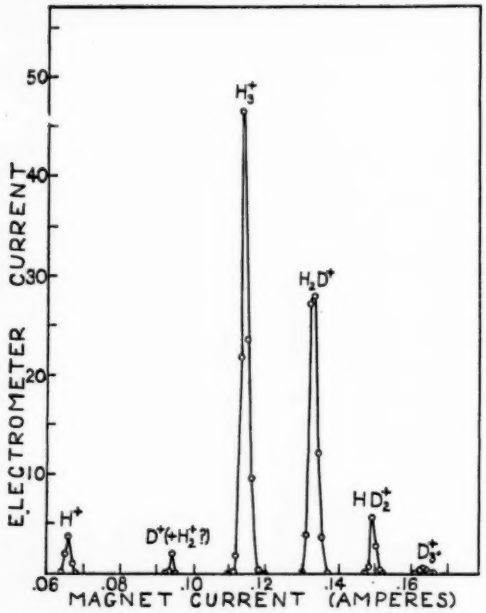

FIG. 3. Aged ions in a mixture containing about 16 percent deuterium.

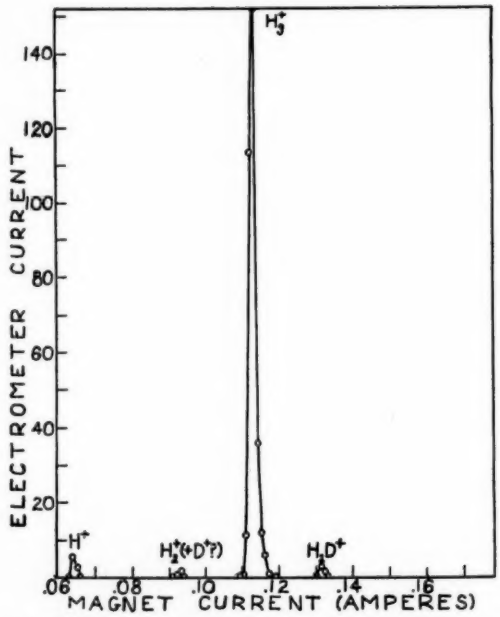

FIG. 4. Aged ions in hydrogen containing about 0.6 percent deuterium.

in Table I for the relative intensities of the ions. The relative heights of the ion peaks bear simple relationships to the ratio of atomic hydrogen and deuterium ($H_3^+/H_2D^+ = h/3d$, etc.), and the percentages h and d should be the same when determined from any pair of peaks. Such calculations indicated, however, that the intensities of the H_3^+ and D_3^+ ions were too large relative to H_2D^+ and HD_2^+. For example, in Fig. 2 the ratio of atomic abundance, h/d, determined from H_3^+/H_2D^+ is 1.08, while from HD_2^+/D_3^+ it is 0.83. Intermediate values of 0.93 and 0.92 are obtained from the ratios H_3^+/D_3^+ and H_2D^+/HD_2^+. The average of all possible combinations is 0.92. These results are typical of some fifteen runs.

It was next supposed that the molecules H_2, HD and D_2 had reached a state of equilibrium at approximately room temperature, and the equilibrium constant K, defined by:

$$K = (HD)^2/[(H_2)(D_2)]$$

had the value[7] 3.28 instead of the straight probability value, 4. It was finally assumed that there was no further preferential grouping when the primary molecular ions combined with neutral molecules to form triatomic ions, by such reactions as:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_2^+ + HD \begin{cases} \rightarrow H_3^+ + D \\ \rightarrow H_2D^+ + H \end{cases}$$
$$H_2^+ + D_2 \rightarrow H_2D^+ + D.$$

Similar reactions were assumed for the HD^+ and D_2^+ ions. The results themselves furnish the only proof that this last assumption is valid.

The ratios of the heights of the peaks no longer bear simple relations to the atomic ratio h/d, but the results are most easily obtained by graphical methods. Table II was prepared showing the ratios of the triatomic ion peaks for various percentages of atomic hydrogen (h) and atomic deuterium (d). This was done by first calculating the percentage of H_2, HD and D_2 molecules present for the various atomic percentages and then adding up the probabilities of formation of the several triatomic ions, taking

TABLE I. *Relative intensities of triatomic ions from ordinary probability, where h and d are the percentages of atomic hydrogen and deuterium, respectively.* ($h+d=100$.)

Ion	Molecular weight	Relative intensity
H_3^+	3	h^3
H_2D^+	4	$3h^2d$
HD_2^+	5	$3hd^2$
D_3^+	6	d^3

[7] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); Urey, Rittenberg and Bleakney, J. Chem. Phys. **2**, 48 (1934).

TABLE II. *Ratios of triatomic ion intensities for various percentages of atomic hydrogen (h) and deuterium (d). $K=3.28$.*

h (%)	d (%)	H_3^+/H_2D^+	H_3^+/HD_2^+	H_3^+/D_3^+	H_2D^+/HD_2^+	H_2D^+/D_3^+	HD_2^+/D_3^+
0	100	——	——	0	——	0	0
5	95	0.0199	0.00112	0.000176	0.0562	0.00882	0.157
10	90	0.0423	0.00501	0.00164	0.118	0.0389	0.328
20	80	0.0948	0.0250	0.0181	0.263	0.191	0.723
30	70	0.1560	0.0688	0.0850	0.441	0.543	1.234
40	60	0.240	0.1620	0.308	0.675	1.29	1.90
50	50	0.357	0.357	1.000	1.000	2.80	2.80
60	40	0.526	0.777	3.25	1.48	6.17	4.17
70	30	0.810	1.840	11.76	2.27	14.53	6.42
80	20	1.380	5.25	55.3	3.80	40.0	10.52
90	10	3.050	25.7	610	8.44	199.5	23.65
95	5	6.37	113.6	5700	17.80	892	50.2
100	0	∞	∞	∞	——	——	——

into account all possible reactions similar to those indicated above. The ratios of these probabilities are then the ratio of the triatomic ion intensities.

From the values given in Table II, curves were plotted with the ratios of the triatomic ion intensities as functions of h or d. These curves were used to determine h and d from the mass spectrograph curves such as those shown in Figs. 1 to 3, assuming the heights of the peaks were proportional to the intensities of the ions. Within the limits of experimental error, the results were then consistent when calculated from the ratio of any pair of peaks, and the fractions of atomic hydrogen or deuterium could be determined in all cases with an estimated error of less than five percent. For example, the average value of h, determined from all possible peak ratios in Fig. 1, is (15.7 ± 0.3) percent; from Fig. 2, (48.5 ± 0.4) percent; and from Fig. 3, (83.7 ± 0.4) percent. The probable errors are calculated from Peter's approximation formula,[8] and may be too small as the individual observations are not completely independent. There was no independent method available for checking the results, but their consistency is believed to furnish sufficient proof of their validity.

In order to make the method outlined above more readily usable for other workers who might wish to analyze mixtures of the isotopes, an attempt was made to devise simple empirical relations to express the results of Table II. The following equations expressing h/d or d/h as a function of the peak ratios, were found to give the correct results to within about one percent over the range of the table:

$$h/d=\alpha(3-0.13\alpha^{-1}), \tag{1}$$

$$\text{For } \beta<1:\ h/d=0.93\beta+0.07\beta^2 \quad \text{(a)}, \qquad \text{For } \beta>1:\ d/h=0.93\beta^{-1}+0.07\beta^{-2} \quad \text{(b)}, \tag{2}$$

$$d/h=\gamma^{-1}\,(3-0.13\gamma^{1}), \tag{3}$$

where $\alpha=H_3^+/H_2D^+$, $\beta=H_2D^+/HD_2^+$, $\gamma=HD_2^+/D_3^+$. Since only three of the six peak ratios shown in Table II are independent, three equations suffice to calculate h/d from any experimental results. The equations, of course, like the table, only apply when the equilibrium constant, K, has a value close to 3.28.

In practice, when the atomic percentages of hydrogen or deuterium are less than 5 or over 95, the straight probability relations given in Table I may be used with negligible error. This results from the fact that some of the peaks become too weak to measure, and the values of Table II approach those given by straight probability for the ratios remaining. In Fig. 4, for example, all but the H_3^+ and H_2D^+ peaks were too weak to be measured, and simple probability gave the average percentage of atomic deuterium from six runs as (0.60 ± 0.03), in agreement with the density measurements on the water used in preparation of the sample.

CONCLUSION

The results of this experiment indicate that a mass spectrograph analysis of the triatomic ions in mixtures of hydrogen and deuterium may be used to determine the abundance of the isotopes in a sample. Simple probability considerations suffice when less than five percent of either atomic hydrogen or deuterium is present, but when the ratio of the two is more nearly equal to unity, the molecular equilibrium constant must be taken into account. The consistency of the results themselves indicates that the formation of triatomic ions from the primary molecular ions is purely a chance phenomenon to a good degree of approximation. That is, there is no preferential clustering of particular atoms in the formation of the triatomic ions.

The writer wishes to express his gratitude to Dr. A. McKellar, Dr. C. A. Bradley and Professor Louis Harris, all of M. I. T., who kindly supplied the samples of heavy water. He wishes especially to thank Professor V. Rojansky of Union College for his aid and helpful discussions on the theoretical aspects of this paper.

[8] F. W. Mellor, *Higher Mathematics*, p. 524, London, 1929.

An Investigation of Adsorbed Films by Means of a Photoelectric Counter

CYRIAS OUELLET* AND ERIC K. RIDEAL, *Laboratory of Colloid Science, Cambridge*

(Received December 30, 1934)

A photoelectric tube counter of special design has been used for investigating adsorbed layers on a gold surface. The high sensitivity of the counter allows accurate measurements of photoelectric thresholds to be made with continuous ultraviolet light from a source of moderate intensity. The variation of the work function φ with the amount of adsorbed material can thus be followed quantitatively and continuously. The formation of gold oxide layers proceeds over definite steps with increases of 0.35 volt in the work function. The adsorption of iodine is reversible and the resulting increase in the work function varies with the iodine pressure according to a Langmuir isotherm, the saturation value being $\Delta\varphi = +0.21$ volt. The adsorption of ethyl alcohol is also reversible, but gives rise to a double threshold, suggesting the existence of liquid islands on the gold surface.

INTRODUCTION

THE effects of gases and vapors both on the intensity and on the threshold of the photoelectric emission of metals have long been recognized as the greatest of the experimental difficulties to be overcome in the measurement of photoelectric thresholds.[1] In spite both of the complexity of the phenomena observed and of the conflicting results obtained it appears clear that a distinction can be made between occluded and adsorbed gases, that the photoemission is affected by external gases only insofar as they are adsorbed on the surface and that an increase in the emission is generally connected with a decrease in the work function and an adsorption of an electropositive gas and *vice versa*. No serious attempt appears to have been made to utilize the photoelectric method for examining the actual behavior of gases and vapors on adsorption as revealed by a change in the photoelectric behavior of the surface.

The extreme sensitivity of a photoelectric counter permits of the evaluation of changes in the photoelectric threshold of metallic surfaces caused by the adsorption of gases or vapors to a high degree of precision $\sim$10A with the aid of a relatively weak continuous source of radiation, and at the same time the shape of the photoemission curves in the neighborhood of the threshold can be explored by this means much more accurately than by the usual photoelectric method.

EXPERIMENTAL

The modified type of Geiger-Müller Rajewsky photoelectric counter[2] constructed for these experiments is shown in Fig. 1. It consisted of a Pyrex glass cylinder 20×6 cm provided with a quartz window Q and a Pyrex cap (l ii). The photon receiver consisted of a cylindrical metal (usually gold) tube C 2 cm long and 1 cm in diameter provided with an axial 2 mm slit for admission of the light. The cylinder C was mounted vertically by a well insulated lead passing through a ground joint plug (a) in the cap. The tungsten anode wire W running down the axis of the metal cylinder was mounted eccentrically on a Pyrex glass frame and connected by well insulated nickel wire to a lead passing through a second ground-glass joint (b) in the cap. By suitable rotation of the plugs (a) and (b) in the cap the wire anode could be inserted along the axis of the photon receiver tube or removed therefrom by passage through the slit. Two fixed leads d and e were used occasionally for heating the metal cylinder and filament. As cathodes metals with thresholds below $\lambda = 3000$A were used, the Pyrex walls provided adequate screening against stray ultraviolet radiation.

A voltage of some 1000–1500 volts is applied through a 10^9 ohm resistance to the electrodes. When an electron is emitted, on its acceleration by the field through a gas at a few cm pressure in the tube the ionization effected by collision gives rise to a small discharge. The resulting voltage impulse is transmitted through a condenser to the grid of an amplifying valve and

* Lecturer at the École Supérieure de Chimie, Université Laval, Quebec, Canada.

[1] For a discussion see Gudden *Licht-elektrische Erscheinungen*, Berlin; Hughes and Dubridge *Photo-electric Phenomena*.

[2] Rajewski, Zeits. f. Physik **63**, 570 (1930); Physik. Zeits. **32**, 121 (1931).

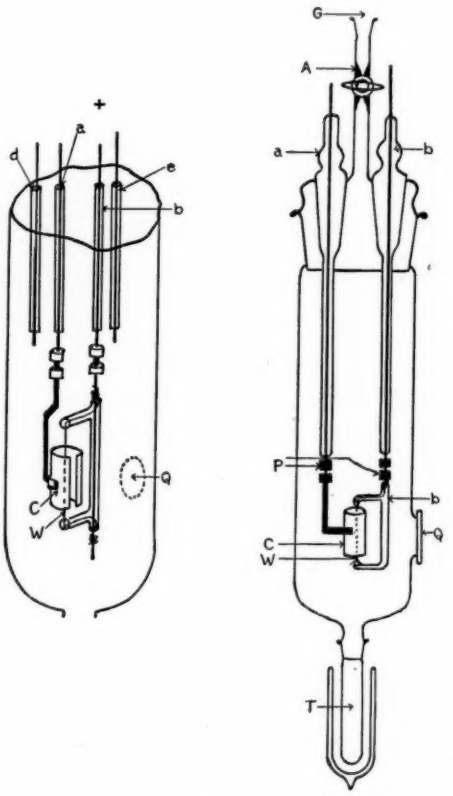

FIG. 1.

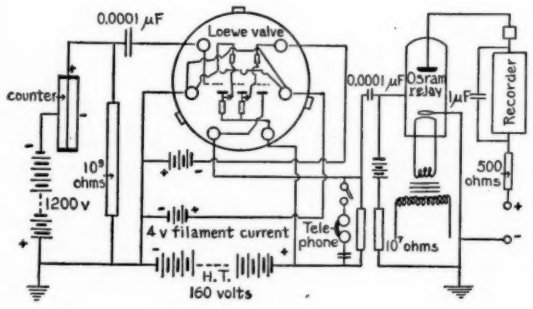

FIG. 2.

recorded on a counter in the usual manner and shown diagrammatically in Fig. 2.

Such glass-contained counters exhibit better working characteristics than ones in which ebonite insulation is provided.[3] The counting rate as a function of the voltage was determined both with ultraviolet light and with a weak RaD source; the latter was also used as control before each run. With the radioactive source constant rates extending over a range of 100–120 volts were easily obtained, whereas with light both the number and size of the impulses were found to increase gradually with the voltage after the sharp initial rise as already noted by Locher.[4] In some cases the voltage plateau consisted of two steps of ranges of about 30 and 100 volts, respectively, with an increase of some 50 percent in the counting rate at the higher potential plateau, a state of affairs apparently favored by the use of light of wavelengths near the threshold; this phenomenon seems to support the view of Locher[4] that electrons with low initial velocities may fail to produce ionization unless they are drawn out by a sufficient field; the presence of steps is thus due to inhomogeneities in the field due either to microscopic cracks or some defect in the geometry of the electrodes. The dark rate in air was found initially to be three per minute; later, due to accumulated radioactive contamination, it rose to a steady value of about 26 per minute, a rate inappreciable to the values obtained when photoelectric measurements were made. As light source a hydrogen lamp consuming 0.3 ampere at 2000 volts was generally employed in conjunction with a Leiss double quartz monochromator. The radiation was found to be uniform in intensity between 3200A, the lowest threshold measured, and 2200A and fell off rapidly at 2100A, the limit of effective transmission of the optical system. Over the range 3200A and 2400A a quartz tungsten filament lamp with a filament temperature of 2800°K was likewise employed. The absence of a marked tail at the foot of the threshold curves shows that the light was sufficiently monochromatic. With an iron arc, very fine slits 0.01 mm could be employed, but it was felt that the sharpness of the thresholds obtained was largely illusory due to the irregular spectral energy distribution and lack of constancy of the source. The counter was connected to a mercury diffusion and Hyvac evacuation system by ground joint connections, a liquid air and cadmium or gold trap being inserted in the line to retain mercury vapor when desired. Oxygen free electrolytic hydrogen and nitrogen and air, the latter purified from dust by passage through olive oil, were stored over phosphoric

[3] Rajewsky, Ann. d. Physik **20**, 13 (1934); Locher, Phys. Rev. **42**, 525 (1932).

[4] Locher, Phys. Rev. **42**, 532 (1932).

anhydride before use. Traces of mercury vapor accidentally introduced into the counter were difficult to remove, filling the bulb with wet oxides of nitrogen for a short time being the most effective method.

In carrying out a run the substance to be adsorbed was introduced into the tube T (Fig. 1) which was then cooled to the temperature of liquid air and the system evacuated. The tube T was then placed in a constant temperature bath to give the desired vapor pressure, and when equilibrium was established the total pressure in the counter was raised to the required pressure for counting by admission of dry gas. The high tension was then applied and the rates of counting with light of a series of wavelengths determined. Counting periods of from one to five minutes, generally one minute, were sufficient. The points on the curves were not determined in their natural sequence but at random, thus rendering any change in the photoelectric behavior of the cathode during the run easily detectable. The chief advantage of the method lies in the high sensitivity of the counter, a beam of only 50 quanta per second falling on the metal could be detected, thus permitting the use of the relatively weak continuous spectrum of hydrogen, very fine slits and a double monochromator. Again, due to the sensitivity of the counter the intensity axis of the threshold curves is greatly elongated and their otherwise asymptotic foot already shows an appreciable slope resulting in a sharper definition of the shape of the foot and of the point at which the curves cut the wavelength axis.

On the other hand, the necessity of using a gas makes it impossible to work with outgassed metals under ideal conditions, and the method is applicable only to systems in which either selective adsorption is predominant or where the vapors may be employed at relatively high pressures. In some cases the possibility of the adsorbed layer being disturbed by the discharge in the counter or by the photons passing through the gas or falling on the surface have to be taken into consideration, e.g., in the presence of the vapor of carbon disulphide. Finally the role of adsorbed films on the wire anode is an all important one for the successful operation of the counter; thus if the gold cathode and wire are cleaned by a discharge in hydrogen at low pressure and the counter subsequently filled with pure hydrogen or nitrogen, no counting is obtained for some time but only a continuous discharge, an effect also observed by Bosch.[5] On introduction of a mere trace of oxygen counting is resumed immediately.

The Photoelectric Behavior of Gold in the Counter

As a preliminary to the measurements of the effects of adsorption the photoelectric behavior of gold was first examined. The threshold of thoroughly outgassed gold at 20°C was found by Morris[6] to lie at 2560A ($\phi=4.83$ volts) and to travel during the process of outgassing from $\sim$ 2100A to 3200A and back to the end value of 2560A a maximum excursion of about 2 volts. For non-outgassed gold Suhrmann and Roy found values of 2597A and 2625A[7] whilst Goetz[8] gives 2800A (4.43 volts) for the thermionic work function at 1050°C. According to Suhrmann[9] the effect of electron bombardment on a specimen of gold is to displace the threshold from 2650–2700A to 2500–2550A, whereas a value of 2900A is reached after passing an electric discharge through hydrogen. Dubois[10] obtained an excursion of the phase boundary potential of 0.3 volt on admission of oxygen, whilst Whalley and Rideal[11] obtained an excursion of 1.56 volts on oxidation of a 'reduced' gold. Our first measurements with gold in air were made in the presence of mercury vapor and gave a sharp threshold at 2650$\pm$5A. Various treatments such as oxidation, reduction, adsorption of alcohol or iodine only effected a temporary alteration in this value to which it returned after removal of the adsorbed material. The presence of this threshold proved to be a sensitive test for mercury vapor and could be obtained at will. The same threshold was obtained with a silver white gold amalgam.

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[5] Bosch, Ann. d. Physik **19**, 65 (1934).
[6] Morris, Phys. Rev. **37**, 1263 (1931).
[7] R. Suhrmann, Zeits. f. Physik **33**, 79 (1925); S. C. Roy, Proc. Roy. Soc. **A112**, 594 (1926).
[8] Goetz, Zeits. f. Physik **34**, 531 (1927).
[9] Suhrmann, Physik. Zeits. **30**, 939 (1929).
[10] Dubois, Ann. de physique **14**, 680 (1930).
[11] Whalley and Rideal, Proc. Roy. Soc. **A140**, 488 (1933).

In the complete absence of mercury vapor it was soon recognized that there were a few definite values to which the work function of gold after various treatments would spontaneously revert in course of time.

The threshold of gold washed after reduction with ethyl alcohol and left to stand in air was found to lie at 2520A (4.90 volts) and seemed to correspond to a stable oxide to which the gold surface eventually reverts in air even after drastic oxidation or reduction.

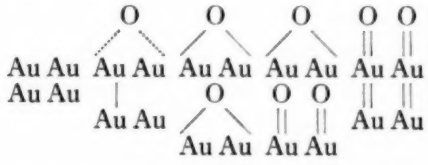
Oxidation by passing an electric discharge in air or oxygen imparts to the gold a characteristic threshold of 2360A (5.25 volts) whilst strong oxidation with nitric acid or heating to redness in air causes the formation of an almost photo-insensitive gold surface with a threshold at *ca.* $\lambda = 2150$A (*ca.* 5.7 volts). By reduction in hydrogen the threshold shifted to longer wavelengths attaining a fairly stable value of 2950A. On re-admission of oxygen at room temperature the threshold slowly returns to the normal value of 2520A an indication of catalytic combination of the hydrogen on the surface. The greatest extension of the threshold in hydrogen was $\lambda = 3050$A ($\phi = 4.02$ volts) obtained by continuous and vigorous reduction by discharge. The values obtained in this manner are compared in Table I

TABLE I.

Author	Treatment	λ_0 Angstroms	ϕ Volts
Morris	Outgassing	~2100	
This work	Prolonged oxidation by nitric acid or heat	*ca.*2170	*ca.*5.6
" "	Oxidation by electric discharge in air	2360	5.25
" "	Normal value in air	2520	4.90
Morris	Outgassing	2560	4.83
Suhrmann	Reduction in hydrogen	2900	4.25
This work	" " "	2950	4.20
" "	Extreme value on reduction	3050	4.02
Morris	Extreme value on outgassing	3200	3.85

with those obtained by other methods. The maximum excursion obtained between the oxidized and reduced forms is *ca.* 1.58 volts comparable to 1.56 volts obtained by Rideal and Whalley and about 2.0 volts by Morris. It is evident that the values obtained with the quantum counter agree closely with those derived by the normal photoelectric or by the thermionic methods and further suggest that the oxidation of reduced gold takes place in two well-defined steps with respective increases of 0.70 and 0.35 volt in the work function, of which the latter was obtained also by Dubois.[10]

It is interesting to note that these regular increments in the work function on progressive oxidation suggest that the work function of clean gold is 4.20 volts and that the increments are directly connected with the change in valency of the surface atoms of gold on oxidation. We obtain the following series:



ϕ volts.	4.20	(4.55)	4.90	5.25	5.6
$\Delta\phi$ volts.		0.35	0.35	0.35	0.35

The excursion of 1.40 volts may be compared with the value of 1.365 volts obtained by A. Gerke and M. Rourke[12] for the potential of what was believed to be the gold auric oxide electrode at 25°C. No higher oxide was detected and the lower oxides were found to be unstable.

From experiments both on the accommodation coefficients of gases at metal surfaces examined by Roberts[13] and from the exhaustive work of Dubridge[14] and of Cassel and Glückauf[15] on the thermionic behavior of platinum it is shown that it is extremely difficult to obtain and maintain a clean surface of a metal for any period longer than a few minutes. The interior of a thin metal wire proves to be a copious source of gas which slowly diffuses out with a relatively high energy of activation. For platinum at least ten hours at 1370°K are required with a temperature coefficient of the order of 2.1 an almost endless period would be necessary at 900°K, the maximum temperature available for gold. A temporarily clean surface can be obtained by flashing or in the case of an oxide film by removal of this film by combustion with hydrogen.

[12] A. Gerke and M. Rourke, J. Am. Chem. Soc. **49**, 1855 (1927).
[13] Roberts, Proc. Camb. Phil. Soc. **30**, 74 (1934).
[14] Dubridge, Phys. Rev. **29**, 451 (1927); **31**, 236 (1928); **32**, 961 (1928).
[15] Cassel and Glückauf, Zeits. f. physik. Chemie **4**, 347 (1932).

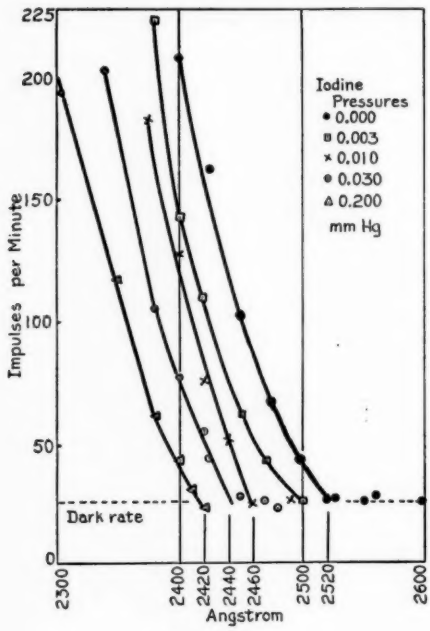


FIG. 3.

THE ADSORPTION OF IODINE ON GOLD

If iodine vapor be admitted to the gold surface in the presence of air, the threshold is displaced towards shorter wavelengths by an amount increasing with the iodine pressure up to a limiting value reached at saturation pressure. The process is readily reversible and in all cases the values of the thresholds could be reproduced within ±5A even after intervals of several weeks during which the gold had undergone various treatments. Some of the curves obtained are shown in Fig. 3.

Only at saturation pressure does the working of the counter become rather critical resulting in less definite results. If the gold be left in iodine at saturation pressure for some hours, much longer periods are required for desorption of the iodine, there is a marked decrease in photoelectric sensitivity suggesting a slow building up of a thick layer which is further confirmed by a gradual darkening of the color of the gold. During desorption gas could be admitted at regular intervals of time and the thresholds quickly estimated before continuing the desorption, a series of operations that could be performed in about three minutes.

Typical results for the process of removal of iodine from a slightly amalgamated gold surface are given in Table II.

TABLE II.

Time in minutes	Before adsorption	0	10	20	30	90
Threshold (A)	2650	2390	2450	2490	2520	2640

The results obtained at a series of iodine pressures are summarized in Table III and Fig. 4.

The curves obtained have the form of the Langmuir adsorption isotherms when $\Delta\phi$ is plotted against the iodine pressure, suggesting that the change in the work function is proportional to the amount of iodine adsorbed. This is probably due to the fact that since even at saturation the alteration in the work function of the gold surface by the adsorbed iodine is relatively small, the effective strength of the adsorbed dipoles must be small, thus no dispersive forces of any considerable magnitude come into play. In the last column of Table III are given the values of $\Delta\phi$ calculated according to the equation

$$\Delta\phi = \bar{\Delta}\phi_m \cdot ap/(1+ap).$$

There is a good agreement between the experimental and calculated figures. According to Campbell[16] at 25°C the dissociation pressure of aurous iodide is 95 percent of the saturation pressure of iodine vapor, thus in agreement with the present experimental data no thick film of surface iodide is formed except near the saturation point and no breaks in the $\Delta\phi$, p curves are

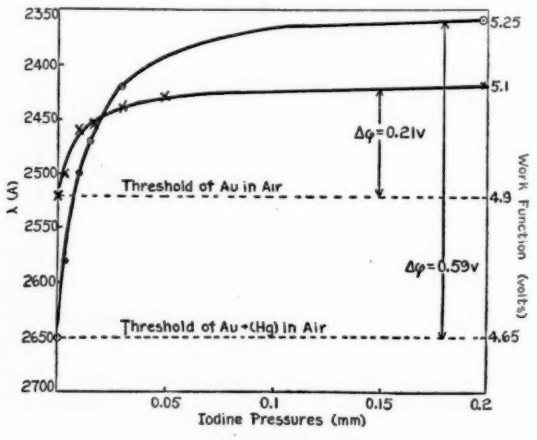


FIG. 4.

[16] F. Campbell, Chem. News **96**, 15 (1907).

TABLE III.

TEMP. OF I_2 (°C)	VAPOR PRESSURE OF I_2 (mm Hg)	THRESHOLD (A)	φ (volts)	$\Delta\varphi$ obs.	$\Delta\varphi$ calc.
					$a=162.5$
	Absence of Hg vapor				$\Delta\phi m=0.21$
	0.000	2520	4.89	0.00	0.00
−20	0.003	2500	4.93	0.04	0.069
−10	0.010	2460	5.02	0.13	*0.13*
− 5	0.017	2455	5.03	0.14	0.15
0	0.030	2440	5.06	0.17	0.17
+ 5.4	0.05	2430	5.08	0.19	0.19
+20	0.2	2420	5.10	0.21	*0.21*
					$a=84.5$
	Presence of Hg vapor				$\Delta\phi m=0.59$
	0.000	2650	4.66	0.00	0.00
−20	0.003	2580	4.78	0.12	0.12
−10	0.010	2500	4.93	0.27	*0.27*
− 5	0.017	2470	5.00	0.34	0.35
0	0.03	2420	5.10	0.44	0.43
+18	0.17	2360	5.25	0.59	0.56

found as in the case of oxygen where one may presume the existence of a number of definite surface oxides. Similar phenomena were observed in the cases both of bromine on gold $\Delta\phi_m=0.32$ volt and of iodine on silver and on a tungsten (WO) surface with respective thresholds of $\lambda_{Ag}=2800$A $\lambda_{WO}=2810$A and changes in the work function at saturation of $\Delta\phi_m$ Ag-I $=0.40$ volt and $\Delta\phi_m$ WO-I $=0.20$ volt, respectively, but the relatively rapid formation of thick films with consequent loss of photoelectric sensitivity at these temperatures rendered the gold iodine system much more suitable for detailed investigation.

THE ADSORPTION OF ORGANIC VAPORS ON GOLD

It is well known that in the case of van der Waals' adsorption of organic vapors by charcoals and by metals the form of the adsorption isotherm is sigmoid and a number of interpretations have been given in explanation of this fact. There is strong evidence for the assumption that the low pressure portion corresponds to a Langmuir adsorption isotherm. On continued increase of pressure this is sometimes followed by a short or long period of pressure increase with but a relatively small increase in the amount of vapor adsorbed. This portion in turn precedes a further steady rise in adsorption with the pressure. Occasionally near the saturation point a marked rise is again noted. These phenomena have been variously interpreted as due to the formation of multimolecular layers, or as due to condensation in microcapillaries. A third view suggests that it marks the transition from a two-dimension "vapor" obeying the Langmuir adsorption isotherm to a two-dimensional liquid phase resulting in the formation of islands of liquid monolayers at the expense of the vapor phase and that it is not until the liquid phase is complete and the pressure almost at saturation that flooding of the capillaries takes place.

It is evident if the third hypothesis be correct that over a more or less extended portion of the p, x curve the surface will be composite in character consisting of patches of two-dimensional vapor and liquid phases, the latter increasing as the pressure increases (isobaric growth will not occur until the liquid phases are large enough to be unaffected by the change in surface tension with the curvature). We might anticipate that the photoelectric thresholds of the surface covered with vapor and liquid phases, respectively, might differ from one another provided that the relative rate of electron emission was greater than the rate of compensation taking place across the composite film to re-establish a surface of uniform potential, and we should thus observe, at any rate with large islands, the phenomenon of a composite surface with two thresholds.

Double thresholds have been found in thermionic emission from sensitized potassium surfaces and also with tungsten.[17] The method of exploring the surface with the aid of a quantum counter is evidently more direct than that derived by the thermionic method as it gives immediate information about both the depth of the depressions in the surface energy barrier and the fraction of the surface they cover.

Preliminary experiments with various vapors in the counter revealed that petrol ether was without effect and that no change in threshold occurred with benzene at 3 mm and 30 mm Hg pressure, chloroform at 2, 5 or 17 mm and carbon tetrachloride at 10 and 25 mm although in all

[17] O. W. Richardson and K. T. Compton, Phil. Mag. **26**, 549 (1913); O. W. Richardson and A. F. A. Young, Proc. Roy. Soc. **A107**, 377 (1925); A. F. A. Young, ibid. **A104**, 611 (1923); H. R. Laird, Phys. Rev. **34**, 463 (1929); H. A. Warner, Phys. Rev. **37**, 233 (1933).

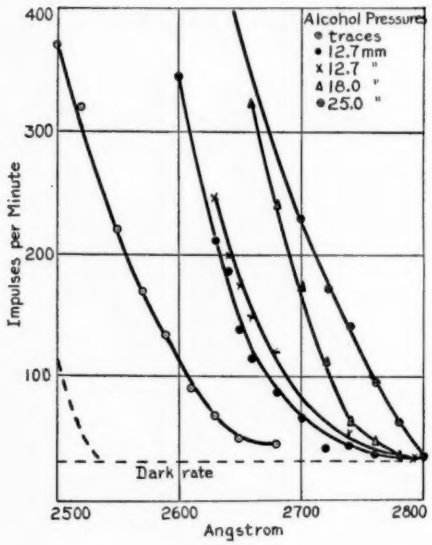


FIG. 5.

three cases the intensity of the emission decreased considerably with rise in pressure. Since these vapors possess absorption bands in this region, the possibilities of a surface action being involved are masked by the screening effect.

Carbon disulphide vapor in the presence of air exhibited an interesting behavior at a weakly amalgamated gold surface. The photoelectric threshold of 2650A was unaltered by the carbon disulphide, but upon irradiation with light within the region $2650<\lambda<2800$A periodic bursts of activity were noted occurring at fairly regular intervals of about one minute. The gold surface in the counter eventually developed a reddish color. Light $\lambda>2800$A is without effect, the transition being fairly sharp. The phenomenon occasionally exhibited fatigue but the activity could be readily restored to the initial conditions by irradiating a few minutes with light of $\lambda<2650$A. The photochemical action involved is probably a surface action since no ionization could be detected in the vapor phase by Hughes[18] in the full radiation of a mercury arc through a quartz window.

The counter works well in ethyl ether alone at a pressure of 60 mm Hg and also in acetone and ethyl alcohol in air. These substances on adsorption bring about a reduction in the work function, but the photoelectric behavior of the surface with variation in the partial pressure of the vapor is quite different from that exhibited by oxygen or the halogens. Starting with a low pressure of alcohol (Fig. 5) there appears at the foot of the curve a tail extending towards longer wavelengths. As the pressure is increased this tail gradually swells and its limit on the λ axis becomes more and more definite until this limit itself becomes the foot of a steeply rising emission at $\lambda=2800$A and can be considered as the threshold of the new surface. The phenomenon is completely reversible. It is remarkable that the value of the shift of threshold $\lambda=2520$A to $\lambda=2800=-0.49$ volt is obtained whether the original gold surface had a threshold value of $\lambda=2650$A due to traces of mercury or even when heavily amalgamated or whether, when mercury is absent, gold in its reduced or one of its oxidized forms is employed. Thus with gold with an oxidized surface with threshold at $\lambda=2360$A (5.25 volts) the shift was -0.49 volt and with gold with a surface in a more reduced state with threshold at $\lambda=2520$A (4.90 volts) (see p. 152) an identical shift of the threshold with the alcohol was obtained. If the alcohol vapor be left in contact with the gold for several hours, a slow reduction of the surface oxide layer occurs as revealed by a shift of its photoelectric threshold to somewhat longer wavelengths, which on standing gradually returned to the normal value obtained in air.

The presence of mercury vapor enhances and stabilizes the photoelectric emission in the region of the tail, although it does not alter the essential features of the phenomenon which appears on mercury free and on heavily amalgamated gold.

Acetone and ethyl ether also give a similar variation in thresholds; some of the curves obtained for the latter substance are shown in Fig. 6. The source was an iron arc.

The two thresholds for the original slightly amalgamated gold (2650A) and for the saturated surface (2800A) are clearly evident, but the definitely step-like character of the curves is partly attributable to the absorption of light by the vapor for both acetone and ethyl ether possess absorption bands in this region.

[18] A. L. Hughes, Proc. Camb. Phil. Soc. **16**, 375 (1911)

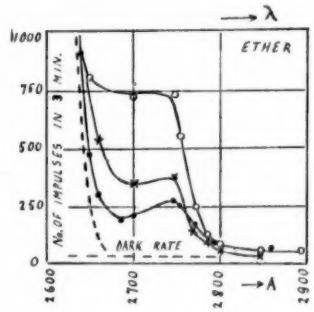


FIG. 6. Adsorption of ethyl ether on gold. Ether pressures: dots, 1 min.; circles, 5 min.; crosses, 15 min.

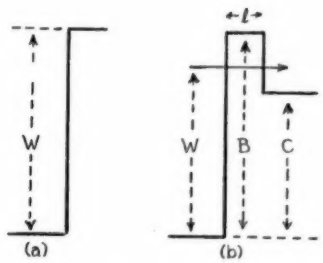


FIG. 7.

If an iron arc which possesses a number of strong emission lines in the neighborhood of $\lambda = 2800$A be employed instead of the hydrogen lamp for the investigation of ethyl alcohol the step-like character of the emission as a function of the pressure displayed by ethyl ether is found in this case also. This permitted of an approximate valuation of the intensity of emission as a function of the alcohol pressure, and was found to be roughly proportional to the square root of the pressure.

It is clear that we are dealing with a case of double thresholds; one of the original surface practically unaffected and the other one -0.49 volt removed from it. It is only the intensity of the emission in the region between the two thresholds which increases with increasing pressure. It seems very likely since the effect is common to the three substances of which ethyl alcohol possesses no absorption bands in this region that the effect is located at the surface of the gold (Fig. 7).

The presence of a positive adsorbed layer would cause the initial surface potential barrier to change from form (a) to (b) and as L. Nordheim and R. H. Fowler[19] have shown the transmission coefficient through an ideal square shouldered hump is finite and equal to

$$\overline{D} = 8(\pi)^{\frac{1}{2}}[(kTC)^{\frac{1}{2}}/B]e^{-2\pi l(B-C)^{\frac{1}{2}}},$$

where B is the total height of the hump and C that of the barrier outside the hump. There is no emission at all for $W < C$. Thus for energies $W > B$ we have the ordinary emission of gold and for $C < W < B$ we obtain the emission tail due to the adsorbed alcohol. If an increase in the alcohol concentration increases $(B-C)$, $\overline{D}$ will increase and the photosensitivity will rise in agreement with experiments. But the tail should also become longer, as C decreases with increasing alcohol concentration and this is not reconcilable with the experimental fact that the threshold of the tail is independent of the pressure of the alcohol. It is clear that leakage through the barrier plays an unimportant role in this case. The most satisfactory hypothesis is to consider the phenomenon as due to the formation of islands and the number or total area of these increasing with the pressure. We thus have two different types of emitting surfaces; that of the bare gold (or covered with vapor) with a full barrier of type (a) and height B and that of the gold covered with a two-dimensional liquid phase with a barrier of type (b) including a thin wall of height $B-C$, through which transmission takes place. As the pressure increases, $B-C$ remains constant, i.e., we still have the same two work functions, but the area of the islands increases until, when the whole surface is covered, the threshold of bare gold has entirely disappeared.

Finally we may note that while the threshold curves generally show an asymptotic approach to the wavelength axis, many of the curves are surprisingly sharp. Since only the electrons in the Sommerfeld levels of maximum energy are responsible for photoelectric emission,[20] sharp thresholds should be expected only at 0°K. As the field gradient on the tube cathode is not very high it seems unlikely that it could assist in pulling out all the electrons of the top level

[19] L. Nordheim and R. H. Fowler, Zeits. f. Physik **46**, 833 (1928); Proc. Roy. Soc. **A122**, 36 (1929).

[20] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

and so sharpen the threshold. Although the steepness of the curves can be accounted for by the magnification of the intensity axis due to the high sensitivity of the counter, the same would apply to the temperature tail and its absence is somewhat remarkable.

Summary

(1) A photoelectric counter has been used for measuring quantitatively the changes in the work function of gold due to adsorbed layers. The high sensitivity of the counter permits an accurate determination of the threshold with monochromatic light from a continuous ultraviolet spectrum of moderate intensity.

(2) The work functions of strongly oxidized and strongly reduced gold differ by 1.58 volts. The oxidation proceeds over two definite steps, with respective increases of 0.35 volt and 0.70 volt in the work function.

(3) The adsorption of iodine vapor on gold at room temperature is reversible and the resulting increase $\sim\Delta$ in the work function varies continuously with the iodine pressure according to a Langmuir isotherm. The value of $\Delta\varphi$ at saturation is 0.2 volt.

(4) The adsorption of ethyl alcohol on gold gives rise to a double threshold consisting of (a) the original threshold of gold and (b) a new threshold corresponding to a decrease of 0.49 volt in the work function, this value being independent of the alcohol pressure. The intensity of the emission at the new threshold increases with increasing pressure. This suggests that the alcohol is condensed in the form of two-dimensional liquid islands, the area covered by these islands increasing with pressure.

We have to thank the Imperial Chemical Industries Limited for assistance in the purchase of the necessary apparatus.

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The Liquid "Structure" of Methyl Alcohol

W. H. ZACHARIASEN, *Ryerson Physical Laboratory, University of Chicago*

(Received November, 8 1934)

Fourier integral analyses of the x-ray diffraction patterns of liquid nonyl and methyl alcohol are made. From these the radial distribution of atoms around any one atom is obtained. On the basis of the radial distribution curves, conclusions are drawn concerning the molecular configuration in the liquid. For nonyl alcohol this analysis confirms the results of Warren. In the case of methyl alcohol the analysis gives strong indication of hydrogen binding (dipole binding) between oxygen atoms of neighboring molecules. The short "life" of a given intermolecular bond in the liquid is emphasized. It is pointed out that the application of the ordinary Bragg equation to the peaks in the diffraction pattern of a liquid has no justification.

Introduction

RECENTLY B. E. Warren[1] published a paper dealing with x-ray diffraction in long chain liquids. He postulated a reasonable "structure" model of these liquids and showed that the diffraction curve calculated on the basis of the model was in agreement with the experimental curves measured by G. W. Stewart and collaborators. Warren considered the length of the chains to be practically unlimited, thereby neglecting the effect which the presence of the end groups of the molecules have on the scattering curve. (It should be mentioned, however, that he gives an interesting explanation of the so-called "inner" peak in the diffraction curve in terms of the length of the molecule.) This effect becomes increasingly important as the number of carbon atoms in the chain decreases. It is therefore not surprising that the diffraction curve calculated by Warren shows little resemblance to the experimental curve of say methyl alcohol.

[1] B. E. Warren, Phys. Rev. **44**, 969 (1933).

It is well known that the alcohols show tendency to glass formation. In order to explain this glass forming tendency on the basis of the general picture of the vitreous state,[2] it was necessary to require the existence of definite bonds between neighboring molecules such that the formation of practically unlimited groups without symmetry and periodicity might be possible. It was to be expected that such definite bonds would exist to some extent even in the liquid state. For obvious chemical reasons this type of intermolecular bond would have to be between hydroxyl groups. Naturally such a binding will affect the radial atom distribution and thus the x-ray diffraction pattern. In the long chain alcohols this effect would be almost completely masked because the carbon-carbon distances predominate. In order to get definite information about possible intermolecular bonds, an analysis of the experimental scattering curve of methyl alcohol was undertaken. For the sake of comparison an analysis was made of nonyl alcohol. In both cases the experimental data of Stewart and Morrow[3] were used.

Analysis of the X-Ray Diffraction Curves

The application of Fourier integral analysis to x-ray diffraction patterns of liquids is due to Zernicke and Prins[4] and Debye and Menke.[5] (Recently Warren and Gingrich[6] have used the same method for powder patterns of crystalline substances.)

If the liquid contains only one kind of atom, and if $p_{(r)}$ is the continuous radial distribution around any one atom,* the intensity, $I_{(s)}$, of the unmodified part of the scattered radiation is given by:

$$I_{(s)}=\frac{e^4I_0}{m^2c^4R^2}\,\frac{1+\cos^2 2\theta}{2}f_{(s)}{}^2N\left[1+\int p_{(r)}\frac{\sin sr}{sr}dr\right]. \tag{1}$$

Here $s=4\pi \sin\theta/\lambda$, $f_{(s)}$ is the scattering power and N is the total number of irradiated atoms in the sample. The integration is over the irradiated part of the sample. The radial function $p_{(r)}$ may be replaced by $4\pi r^2\rho_0+q_{(r)}$, where ρ_0 is the average density of the sample in atoms per unit volume. The function $q_{(r)}$ thus represents excess (or deficit) of actual radial distribution as compared to the average. Eq. (1) may then be written:

$$I_{(s)}=K\frac{1+\cos^2 2\theta}{2}f_{(s)}{}^2N\left[\int 4\pi r^2\rho_0\frac{\sin sr}{sr}dr+1+\int q_{(r)}\frac{\sin sr}{sr}dr\right] \tag{1'}$$

where K is an abbreviation for $e^4I_0/m^2c^4R^2$. For all practical experimental set-ups the first integral will be zero unless $s=0$, in which case it is equal to N. Remembering that

$$I_{\substack{(s)\\ s=0}}=K\frac{1+\cos^2 2\theta}{2}{}_{\theta=0}N^2f_{\substack{(s)\\ s=0}}{}^2$$

one finds:

$$I_{\substack{(s)\\ s\neq 0}}=K\frac{1+\cos^2 2\theta}{2}Nf_{(s)}{}^2\left[1+\int_0^\infty q_{(r)}\frac{\sin sr}{sr}dr\right]. \tag{2}$$

Solving for $q_{(r)}$ by the Fourier integral theorem:

$$q_{(r)}=\frac{2r}{\pi}\int_0^\infty s\left[\frac{I_{(s)}'}{K(\tfrac{1}{2}+\cos^2 2\theta/2)Nf_{(s)}{}^2}-1\right]ds, \tag{3}$$

where $I_{(s)}'$ is the unmodified scattering curve apart from the direct beam ($I_{(s)}'=I_{\substack{(s)\\ s\neq 0}}$). The observed intensity curve is readily corrected for modified radiation and Eq. (3) put upon an absolute basis through a simple procedure described by Warren and Gingrich (reference 6). The $q_{(r)}$ curves for methyl and nonyl alcohol are shown in Fig. 1. The scattering of the groups CH_3, CH_2 and OH was considered equivalent to

[2] W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

[3] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

[4] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).

[5] Debye and Menke, *Ergebnisse der Techn. Röntgenkunde II.*

[6] Warren and Gingrich, Phys. Rev. **46**, 368 (1934); Warren, J. Chem. Phys. **2**, 551 (1934).

* If all the atoms are not structurally equivalent, $p_{(r)}$ will represent a weighted average of the individual density functions.

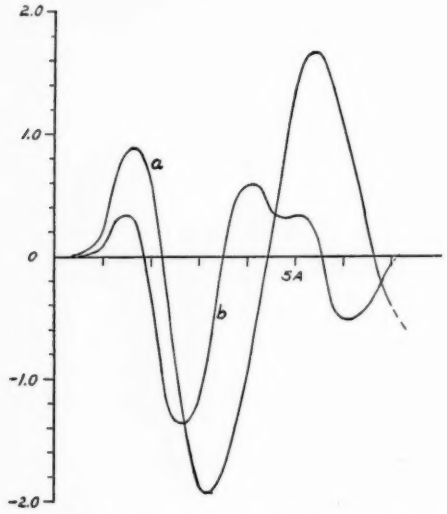

FIG. 1. The $q_{(r)}$-curves of nonyl alcohol (curve *a*) and of methyl alcohol (curve *b*) are shown.

that of oxygen atoms, so that the two liquids to this approximation consist of only one kind of scattering centers. The total radial atom distribution is obtained by adding $4\pi\rho_0 r^2$ to the q_r-curve. The density, ρ_0, of the two substances is 0.030 atom per A^3 for methyl alcohol and 0.0348 atom per A^3 for nonyl alcohol.

DISCUSSION OF THE RADIAL DISTRIBUTION CURVES

A. Nonyl alcohol

If we compare the $q_{(r)}$ curve for nonyl alcohol with the corresponding curve constructed by Warren from his structure model (Fig. 2 of Warren's article), the striking agreement is apparent. Indeed, our result represents a most conclusive proof of the correctness of Warren's picture of the structure in the long chain alcohols.

TABLE I. *Number of atoms between spherical shells.*

r	From $q_{(r)}$ curve	According to Warren's model
0–1A	0.2	0
1–2A	1.8	2 at 1.54A
2–3A	2.0	2 at 2.5A

The comparison of Table I serves to emphasize the quantitative agreement.

The peak in the q_r curve at about 1.6A corresponds to the shortest C–C distance in any one chain (1.54A).* The peak at 5.4A on the other hand corresponds to the shortest mean distance between carbon atoms of neighboring chains.

B. Methyl alcohol

To our approximation, methyl alcohol, CH_3-OH, should show only one intra-molecular distance, which would approximately correspond to the C–O distance. According to Pauling's[7] radii the C–O distance is 1.43A. The peak in the $q_{(r)}$ curve at about 1.5A is due to this distance. The quantitative agreement is quite satisfactory. Evaluation of the integral

$$\int_{r_1}^{r_2} [4\pi\rho_0 r^2 + q(r)]dr$$

gives 0.1 atom in the range $0 \leq r \leq 1$A and 1.1 atoms in the range $1\text{A} \leq r \leq 2$A.

If the molecules were held together by the usual van der Waals forces all interatomic distances between molecules would be fairly large. Thus we would expect the number of atoms between $r=2$A and $r=3$A to be approximately zero. The $q_{(r)}$ curve, it is true, goes down to a minimum at about 3A; but the number of atoms between 2 and 3A comes out 1.3. Now the closest distance between methyl groups of different molecules is of the order of 4.0A.[8] For chemical reasons it is hard to imagine any binding with resulting small distances between methyl and hydroxyl groups. We are therefore forced to the conclusion that every hydroxyl group is linked to the hydroxyl groups of two neighboring molecules at a distance of roughly $2\frac{1}{2}$A. Our analysis thus strongly indicates the presence of hydrogen bonds between oxygen atoms of neighboring molecules, similar to the hydrogen bonds between neighboring radicals in H_3BO_3, KH_2PO_4 and $NaHCO_3$.[9] Every hydrogen atom is thus linked to two oxygen atoms; undoubtedly it is linked more strongly to one of the oxygen atoms than to the other, so it

* It should be noted that the peak at 1.6A is somewhat influenced by the fact that the observed scattering curve breaks off at $s=3.7$.

[7] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

[8] A. Müller, Proc. Roy. Soc. **A120**, 437 (1928).

[9] W. H. Zachariasen, Zeits. f. Krist. **88**, 150 (1934); J. West, Zeits. f. Krist. **74**, 306 (1930); W. H. Zachariasen, J. Chem. Phys. **1**, 634 (1933).

still would be justifiable to talk about hydroxyl groups. Naturally if we wish to characterize the nature of these hydrogen bonds, we should employ the term dipole binding.

It must be emphasized that we do not believe that any one of these intermolecular hydrogen bonds persists in the liquid for an indefinite time. We expect rather that a given bond persists for a limited length of time (the duration being a function of temperature), that the bond then is broken and a new bond formed with another molecule. In other words, if we pick out a molecule at random, the probability of finding at a given instant hydrogen bonds between this molecule and two neighboring ones is appreciable; but there is no certainty. For general reasons this probability will decrease with rising temperature in the liquid.

The hydrogen binding between neighboring molecules is shown schematically in Fig. 2. Because of this binding the molecule under consideration can have no other immediate neighbor molecules in the right-hand solid angle of approximately 2π (see Fig. 2). The neighboring molecules within the solid angle of 2π to the left must point their methyl ends towards the molecule considered. Treating the methyl groups as approximately spherical there would be roughly six neighboring molecules in the space to the left. This would produce a peak in the $q_{(r)}$ curve at a value of r corresponding to the methyl-methyl distance. Obviously the peak at about 4.1A has this origin. This value compares favorably with the methyl-methyl distance of 4.0A found by Müller in the *n*-hydro-carbons. The distance from the oxygen atom of the molecule considered to the same six methyl groups would lie between 4.5 and 5.6A, with an average of about 5.1A. The peak in the $q_{(r)}$ curve for this value of r is thus accounted for.

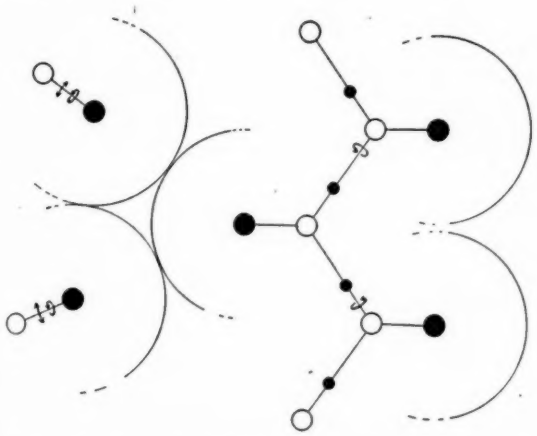

FIG. 2. A schematical picture of the molecular configuration in methyl alcohol is given. Carbon atoms are represented by large filled circles, oxygen atoms by large open circles and hydrogen atoms of the hydroxyl groups by small filled circles. The effective radius of the methyl group is indicated by the half circles around the carbon atoms. Only two of the six neighbor molecules in the left-hand part of the diagram are shown. The angle between the two hydrogen bonds is taken to be 110°, and the closest oxygen to oxygen distance is assumed to be 2.6A. The closest carbon to oxygen distance is 1.4A.

Naturally we have to expect that also these neighbor molecules are constantly changing. Because of the weakness of the bonds between the methyl groups the time any one molecule will spend as neighbor of a given molecule must be extremely short, and the state of affairs may perhaps best be pictured as a reflection of the molecules when approaching the potential hill around the molecule considered. Hence it is impossible to talk about the existence of atomic planes, only the probability of interatomic distances can have significance, and this is indeed sufficient to account for the existence of x-ray diffraction in liquids.

It is well known that many experimenters have tried to gain information about the liquid state by a straightforward application of the ordinary Bragg equation to the peaks in the diffraction pattern. The "spacings" obtained in this manner naturally have no significance, except insofar as they may be re-interpreted in terms of interatomic distances by means of the extreme values of the function:

$$\sin sr/sr[=\sin [2\pi r/d]/2\pi r/d].$$

The significance of the results of this investigation for the glass forming tendency of the alcohols will be taken up for discussion in a future article dealing with organic glasses in general.

The Vitreous State*

W. H. ZACHARIASEN, *University of Chicago*
(Received January 15, 1935)

1. The General Applicability of My Theory for the Structure of Vitreous Solids

IN a recent article Hägg states that my theory for the structure of vitreous solids[1] cannot furnish an explanation of glasses in general, not even for oxide glasses in general. Hägg thinks that my viewpoint is adaptable only to cases where the oxygen polyhedra form three dimensional networks. This statement is due to a serious misunderstanding of my paper. My conception of the atomic arrangement in vitreous solids in general were put forth in Section 2 of my paper. It may be stated briefly: The glasses are built up of extensive three dimensional networks without symmetry or periodicity, these networks being in other respects essentially the same as the ones we find in the corresponding crystals. This picture of the structure of glass certainly has a general enough application. Due to the great variety of glasses it is difficult to give a much more detailed picture for the general case. Indeed, Hägg has been confronted with the same difficulty. Only by applying the general principles on specific types of glasses did I succeed in arriving at a detailed picture of the atomic arrangement, then, of course, applicable to those specific types of glasses only. This is what I did for the oxides in Section 3 of my article. For this class of substances I was able also to take up for discusssion the problem of the conditions under which such vitreous networks could exist. These conditions were in fact derived. Now all the oxides which were known to occur in vitreous forms (and possibly a few other oxides which I enumerated) actually did satisfy these conditions. Similarily I could show that BeF_2 should be the only pure fluoride which could exist in the glassy state. In Section 4 of my article I discuss to some extent general oxide glasses. The conditions for the existence of such glasses were given on page 3848. They do not imply, as Hägg seems to believe, that the so-called vitreous framework has to have three dimensional extension. That I have not even had this in mind, is clear from the statement on page 3849: "It may be expected quite generally that the glasses would have the most advantageous properties if the tetrahedral or triangular networks had three dimensional extension." It is true, however, that I proceed to give a more detailed picture only for this type of oxide glasses, a fact which probably has been responsible for Hägg's misunderstanding.

It is apparent from my paper that I avoided "explaining" the structure of glass in terms of the conditions in the melt, rather I made correlations to the crystalline state. It is in my opinion no real progress to present a theory for the structure of glass in terms of the equally unknown structure of the liquids.

2. Comparison Between Hägg's General Theory and My Own

A. The structure of the vitreous solids

It has been known for a long time that the tendency to glass formation was closely connected with the viscosity of the melt. Hence the tendency to glass formation should be related to the size of the molecules or groups present in the melt. This idea Hägg presents in a more definite form: A melt will show tendency to glass formation if it contains large or irregular groups. Provided this criterion is correct (we shall discuss that point in the next section), it gives a general explanation of how glasses can be formed in terms of the structure of the melt. In itself this gives no picture of the atomic arrangement in the vitreous solids. Hägg's idea is now that the glass is built up of the same entities as were present in the melt, i.e., in the case of a melt containing only one type of groups, the glass would be an aggregate of these large or irregular groups. Hägg is rather vague concerning the structure of any one such fragment; it appears that it need not be crystalline, although it would not be in disagreement with his ideas if it were.

* Comments on the article by Gunnar Hägg, *The Vitreous State*, J. Chem. Phys. **3**, 42 (1935).

[1] W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

He does not discuss the nature of the aggregate and its bearing on the transparency. Hägg's viewpoint for such glasses (e.g., vitreous oxides, organic glasses, element-glasses) is not identical with mine.

If the melt contains small regular groups or single atoms in addition to the large or irregular groups, Hägg's viewpoint would lead, not to an aggregate of smaller fragments, but to one (or a smaller number) continuous medium, in which the large or irregular groups were cemented together by the remaining constituents. Such a conception would be in formal agreement with my general principles. Indeed, there would be no significant difference of opinion between us. I must admit at this point that I have given a *detailed* picture of the atomic arrangement only for glasses in which the groups are practically unlimited in three dimensions. I did not in my paper present a detailed picture in the case that the groups are unlimited in one or two dimensions. The requirement of non-periodicity would, however, for such glasses lead to Hägg's model, with minor modifications.

B. The conditions for glass formation

According to Hägg the general condition for glass formation is the presence in the melt of large or irregular groups, while according to my viewpoint it depends upon whether extensive networks without symmetry and periodicity are possible. Obviously my condition is considerably more restricted. It is fairly evident that substances satisfying my condition necessarily will satisfy that of Hägg, while the reverse is by no means true.

Let us consider the pure oxides as a concrete example. In order to give a fundamental explanation of the glass-forming tendency of the oxides, Hägg has to prove that large or irregular groups are present only in the melts of those oxides which are known to form glass. Hägg has given no such proof, although he has touched the problem in his article. Thus Hägg seems to believe that a crystal of BeO upon melting would dissociate into very small groups because of a more or less ionic type of binding, whereas larger groups would exist when crystalline silica is melted because of a more homopolar binding. Let us assume that Hägg will be able to furnish the required proof. In view of my results for the oxides it is then likely that the conditions for the existence of large groups (not small irregular ones) in melts of pure oxides will become identical with my conditions for the existence of networks lacking symmetry and periodicity, as given in Section 3 of my original article.

The difference between our viewpoints is perhaps best illustrated by the example of H_3PO_4 mentioned by Hägg. In order that this compound be able to form a glass according to Hägg, larger groups than $(PO_4)^{-3}$ must be formed. According to my viewpoint I must with Hägg explain the formation of larger groups; but *in addition* I have to show that such larger groups can be formed *without symmetry and periodicity*. The cause of the formation of larger groups in H_3PO_4 is the presence of the hydrogen atoms. As in H_3BO_3, KH_2PO_4 or $NaHCO_3$ the individual PO_4 radicals are undoubtedly linked together by hydrogen atoms so as to form a practically unlimited three dimensional network. We know, however, from crystal structure results that the hydrogen atom lies midway between two oxygens belonging to two different radicals. Hence we have the possibility of a random orientation of the PO_4-tetrahedra around a given hydrogen bond, and under those conditions it is possible to have a practically unlimited three dimensional network lacking symmetry and periodicity. (Compare the discussion of SiO_2 in my original article.)

I do believe that Hägg's condition is too general, and that he will find it necessary to impose additional conditions which will reduce his theory to mine of two years ago.

Hägg's statement in the summary: "The glass-forming tendency . . . seems to be especially large when the corresponding crystals contain radicals or molecules unlimited in one or more dimensions" is again too general. It is true, of course, that crystalline SiO_2 contains polymerized molecules unlimited in three dimensions, but so does also crystalline TiO_2 or BeO for example, where there is no tendency to glass formation.

The Photodissociation of Some Polyatomic Molecules

YOSISIGE HUKUMOTO, *Physical Institute, University of Sendai, Japan*

(Received December 30, 1934)

A continuous absorption spectrum without a neighboring band spectrum and a convergence limit was investigated in the region of the ultraviolet of a number of polyatomic molecules: Halogen alkyls, alcohols, mercaptans, cyan compounds and other miscellaneous compounds. The energy of dissociation was, in each case, calculated from the absorption edge, considering the probable mechanism of the photodissociation process. Some remarks are given on the relationship between the dissociation energy of the bond and the structure of the molecule. Finally, some consideration is given to the Raman effects and infrared spectra as related to the bond energy of the molecules.

THE correlation of the absorption spectrum of a molecule with its photochemical behavior has been the subject of a number of recent investigations. Spectroscopic investigations have yielded a great deal of interesting and useful information regarding the nature and strength of bond in polyatomic molecules. It can be said that the investigation of the spectra of polyatomic molecules is at present an important problem of chemical physics.

Within recent years, the author has investigated a series of absorption spectra of various groups of polyatomic molecules. Comparatively few measurements on such absorption spectra of polyatomic molecules are on record. Herzberg and Scheibe,[1] Iredale and Mills,[2] Henrici[3] and others have studied some halogen alkyls. Leighton, Cray and Schipp,[4] and others have studied some alcohols. In the following paper the author describes a more complete examination of the continuous absorption spectra of many alkyl halides, alcohols and other compounds, and several features already established are outlined.

I. EXPERIMENTAL

The substances used in this investigation are liquids at ordinary temperatures, are colorless, and the greatest care was taken to obtain pure products. The substances indicated by prefixing *K*, *M*, *F* and *T* were supplied by Schering Kahlbaum A. G., by E. Merck, by Dr. Fraenkel and Dr. Landan and by the Takeda Pure Chemicals Ltd. (Japan), respectively. The remaining liquids investigated were obtained from other reliable sources.

The absorption vessels were cylindrical glass tubes 100 cm long and 4 cm in diameter with polished quartz ends cemented on. The liquid was introduced into the apparatus through a side tube, cooled by liquid air or ice salts while sealing off and evacuated to as low a pressure as possible (10^{-3} mm). And then after vaporizing the liquid in a preliminary expansion chamber, the vapor was admitted through the side tube into the absorption tube as much as possible. Cooling and re-evacuating, the process was repeated in order to clear up any traces of impurity. And then a series of observations was carried out at various vapor pressures and with fresh preparation of the vapor. The continuous source used was a hydrogen discharge tube. The spectrograph was a Hilger instrument E 31. Ilford special rapid plates were used, and in order to obtain a great sensibility in the far ultraviolet, they were oiled with a light transformer oil which was found to be suitable for the purpose.

By increasing the pressure of vapor up to the maximum, seven spectrograms were taken in succession on each plate in the same exposure. At the long wave limit there is, in general, a fairly sharp transition to apparently complete absorption. The estimation of the absorption limits was made on the plates by purely visual and photometric methods.

II. RESULTS

In the case of each vapor only continuous absorption was found, and a careful search failed to

[1] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie **B7**, 123 (1930).
[2] T. Iredale and A. G. Mills, Proc. Roy. Soc. **A133**, 430 (1931).
[3] A. Henrici, Zeits. f. Physik **77**, 35 (1932).
[4] P. A. Leighton, R. W. Cray and L. T. Schipp, J. Am. Chem. Soc. **53**, 3017 (1931).

TABLE I.

	Molecules	Absorpt. limits (A)	Diss. energies (kcal./mole)
	CCl_4	2380	117.1
	$CHCl_3$	2300	121.3
	CH_2Cl_2	2260	123.4
	CH_3Cl	2240	124.5
	C_2H_5Cl	2225	125.1
(K)	CH_2CHCl_2	2180	128.1
(T)	CH_2ClCH_2Cl	2240	125.1
(M)	$CHCl_2CH_2Cl_2$	2330	119.7
	$CH_2ClCHCl_2$	2180	128.0
(K)	C_2Cl_4	2520	110.4
(K)	C_2HCl_3	2460	113.5
(K)	CHClCHCl	2370	117.1
	n-C_3H_7Cl	2230	125.1
	iso-C_3H_7Cl	2160	129.2
(K)	C_3H_5Cl	2300	121.2
	n-C_4H_9Cl	2290	121.3
	tert-C_4H_9Cl	2215	126.0
	iso-$C_5H_{11}Cl$	2200	126.9
(T)	CH_3OH	2130	133.6
(T)	C_2H_5OH	2070	137.5
(M)	n-C_3H_7OH	2020	140.9
(T)	iso-C_3H_7OH	2020	140.9
(K)	n-C_4H_9OH	2005	141.9
(K)	iso-C_4H_9OH	2015	141.2
(K)	sec-C_4H_9OH	2030	140.2
(K)	tert-C_4H_9OH	2015	141.2
(K)	n-$C_5H_{11}OH$	2000	142.3
(K)	iso-$C_5H_{11}OH$	2020	140.9
(K)	sec-$C_5H_{11}OH$	2130(?)	133.6
(K)	tert-$C_5H_{11}OH$	2015	141.2
(K)	n-$C_6H_{13}OH$	1995	142.7
(K)	n-$C_7H_{15}OH$	1985	143.4
(M)	n-$C_8H_{17}OH$(p)	1970	144.5
(M)	n-$C_8H_{17}OH$(sec)	1960	145.2
(F, L)	n-$C_{10}H_{21}OH$(p)	1895	150.2
(T)	n-$C_{12}H_{25}OH$	1870	152.2
(M)	$CHBr_3$	2690	95.4
(K)	CH_3Br	2660	96.4
	C_2H_5Br	2580	99.8
	CH_2BrCH_2Br	2705	102.7
(K)	$CHBr_2CHBr_2$	2460	105.2
(F, L)	CHBrCHBr	2640	97.3
	n-C_3H_7Br	2540	101.6
	iso-C_3H_7Br	2520	102.4
(T)	C_3H_5Br	2740	93.4
	n-C_4H_9Br	2460	105.2
	sec-C_4H_9Br	2360	110.1
	tert-C_4H_9Br	2660	96.5
	iso-C_4H_9Br	2440	106.1
	iso-$C_5H_{11}Br$	2260	104.1
(K)	CH_3CN	2160	131.8
(K)	C_2H_5CN	2160	131.8
	$ClCH_2CN$	2200	129.4
(K)	CH_3SH	2780	102.4
(K)	C_2H_5SH	2750	103.5
(K)	C_3H_7SH	2600	109.5
(F, L)	C_4H_9SH	2590	109.8
(T)	$C_6H_5CH_2OH$	2100	135.5
(T)	$C_6H_5(CH_2)_2OH$	1900	149.8
(T)	$C_6H_5(CH_2)_3OH$	1900	149.8
(T)	$C_6H_5CH_2Cl$	2200	129.4
(F, L)	$C_6H_5CH_2Br$	2380	119.6
(T)	$C_6H_5CH_2CN$	2250	126.5
	CCl_4	2380	117.1
(K)	$SiCl_4$	2160	129.3
(K)	$TiCl_4$	3380	81.7
	$SnCl_4$	2820	98.7

detect any discrete bands, when the absorbing vapor was sufficiently pure. With increasing pressures a continuous absorption starting at higher frequencies gradually extends towards longer wavelengths, and then remains fixed as the vapor pressure is still further increased. The thresholds for these continua at the highest pressures used, are tabulated in Tables I and II.

In the alkyl iodides two or three absorption regions were found, in the other compounds only one region, undoubtedly for the reason that the analogous second and third region falls below the spectral region covered by the use of a quartz spectrograph. The positions ($\lambda_{1,\ 2,\ 3}$) of the absorption maxima are given in Table II.

TABLE II.

	Molecules	Absorpt. limits (A)	Diss. energies (kcal./mole)	Absorpt. max. (λ_1)	Absorpt. max. (λ_2)	Absorpt. max. (λ_3)	ν_2 (max.)$-\nu_1$ (max.) cm^{-1}
(K)	CH_2I_2	3320	64.2	2860	2460	2210	5700
	CH_3I	3100	70.2	2520*	2180*		6100*
	C_2H_5I	3260	65.7	2550*	2180*		6600*
(T)	n-C_3H_7I	3060	71.4	2510	2180		6100
	iso-C_3H_7I	3100	70.2	2520	2110		7700
(T)	C_3H_5I	3380	62.6	2650	2300		5900
	n-C_4H_9I	3060	71.4	2510	2200		5600
	iso-C_4H_9I	2980	63.9	2520	2130		7200
	sec-C_4H_9I	2960	78.0	2550	2140		7500
	tert-C_4H_9I	3170	71.3	2660	2200		7800
	iso-$C_5H_{11}I$	2900	76.5	2520	2120		7500

* Observed only in the case of thin liquid film.

The absorption of very thin liquid films and liquid layers was also investigated. A layer of the liquid 5 mm in length was used. Most of the absorption limits shift towards the less refrangible side. In the case of liquid films, with iodides, first and second absorption maxima were observed in the ultraviolet region.

In recent years, a great deal seems to have been cleared up with regard to the heat of dissociation and the dissociation products, in the case of the simpler molecules. The appearance of the continuous absorption is evidence for the dissociation of the molecules. The threshold for the continuous absorption is employed to determine the energy of bonds of C−halogen, C−OH, C−CN, etc. The different continuous regions of absorption for the same molecule are supposed to be associated with its optical dissociation into products in the various energy states.

This being the case, we may calculate from the long wave limit of the absorption region an upper limit for a dissociation energy of the molecule. But, before calculating the dissociation

energy of the molecule, we must consider the nature of the dissociation products. Several attempts have been made to demonstrate the nature of these products, but unfortunately they have not been successful. No direct proof has yet been forthcoming that the metastable atoms are actually produced in the photodissociation.

(1) Halogen alkyls

The most probable mechanism for the photodissociation corresponding to the first absorption region, seems to be a decomposition into a normal alkyl residue and a metastable halogen atom. And the upper limit of the energy of the carbon-halogen bond was estimated from the long wave absorption limit. The results are given in Tables I and II. The second or third absorption region may correspond to the photochemical dissociation into a slightly excited alkyl and a metastable iodine atom. Each difference ν_2(max.) $-\nu_1$(max.) for all investigated iodides are given in Table II. It may be worth while to notice that the values of ν_2(max.)$-\nu_1$(max.) are nearly constant. Henrici has observed the second and third absorption maximum only in CH_2I_2 and not in mono-iodides, and he proposed a mechanism for the dissociation by interpreting the second absorption region, that is $CH_2I_2+h\nu \rightarrow CH_2I^*+I^*$. According to our results, the second maximum of absorption is observed in all mono-iodine compounds, and his interpretation is not valid. It is worthy of note, on the other hand, that $\nu_2-\nu_1$ is about $5500\sim7800$ (cm^{-1}), as shown in Table II, and nearly equal to $2^2P_{3/2}-2^2P_{1/2}=7600(cm^{-1})$, as in the case of NaI.[5] This seems to throw some doubt on the correctness of the interpretation given above.

(2) Alcohols, cyanic and hydrosulphide compounds

Generally the radicals OH and CN are considered to be pseudo-halogens, and the mechanism of photodissociation is simply considered to be

$$C_nH_{2n-1}OH + h\nu \rightarrow C_nH_{2n-1} + OH^* \ (?)$$
$$C_6H_5CH_2OH^{6} + h\nu \rightarrow C_6H_5CH_2 + OH^* \ (?)$$

analogous to a halogen alkyl. So the dissociation energy in Table I, calculated from the absorption edge, must be modified, if the energy necessary to excite the OH radical is known.

In regard to cyanic compounds, it is simply considered as $CH_3CN+h\nu \rightarrow CH_3+CN$, or $ClCH_2CN+h\nu \rightarrow CH_2Cl+CN$. According to the investigation of Mooney and Reid[7] of the ultraviolet absorption spectra of cyanogen halides, CN* has an excitation energy of 41 or 73 kcal. In this case, therefore, the photodissociation would not produce CN* molecules, as we consider the dissociation energy calculated from the thermochemical data. In regard to the hydrosulphide compounds, it is also considered as $C_2H_5SH+h\nu \rightarrow C_2H_5+SH$. But a definite conclusion has not yet been arrived at with regard to the heat of dissociation and the dissociation products.

(3) XCl_4 type molecules (CCl_4, $SiCl_4$, $TiCl_4$ and $SnCl_4$)

The most probable mechanism for the photodissociation is considered to be $XCl_4+h\nu \rightarrow XCl_3+Cl^*(2^2P_{1/2})$.

The respective heat of dissociation can be calculated from the published data on the respective heat of combustion of the aliphatic organic compounds. The calculated values are compared with the results given in Tables I and II. The data of the results are not so accurate as the absolute values, but they seem to have a definite physical meaning as *relative values* and to be of sufficient interest to warrant publication.

III. Bond Energy and Molecular Structure

The modification of the characteristics of the bonds of C−halogen, C−OH, C−CN, etc., that is, (1) the effect of the halogen substitution for another atom or radical on the bond energy, (2) the effect of a lengthening of the hydrocarbon chain on the bond energy, and (3) the effect of a branching of the hydrocarbon chain upon the bond energy, etc., were studied. Summarizing the

[5] A. Terenin, Zeits. f. Physik **44**, 713 (1927).

[6] In the benzene derivatives, it is seen that a system of narrow, sharp bands occurs from *ca.* 3000A towards the shorter wavelength region. This spectrum may be attributed to some aromatic binding and may receive a further investigation.

[7] R. B. Mooney and H. G. Reid, Nature **128**, 271 (1931).

results of this paper, some concluding remarks are here given.

(1) It is obvious from the results of many sequences of compounds that in any case of the halogen alkyl, the energy of the carbon-halogen bond increases rapidly from iodide to bromide to chloride, that is with the decreasing of the atomic weight. This is in accord with other known chemical relations. In the other cases, as shown in Tables I and II, such a tendency is also observed.

(2) The C−halogen bond energy decreases successively as the halogen atom is substituted for hydrogen atom in any case of the halogen alkyls. So bond energy has the maximum value for a monohalogen compound. Such a regularity has also been detected by Henrici.[3]

(3) The C−OH bond energy increases successively as we go up the series of normal alcohols, varying within narrow limits from compound to compound. Such a regularity has also been detected in the case of the halogen alkyls and other compounds.

(4) In the case of the isomers, it does not seem possible to detect any regularity among the energies of the C−halogen and C−OH bonds. But it seems to assume the maximum values for the corresponding normal compounds.

It is doubtful whether all the cases of regularities here mentioned have a genuine physical meaning, and some one may be merely provisional in character. Much more experimental data are needed, especially of a quantitative nature, in order to reach a definite conclusion. But these remarks may give some means of advancing our knowledge of these polyatomic molecules.

IV. Comparison with the Raman Spectra and Infrared Spectra

In connection with the study of the absorption spectra in the ultraviolet region, it may be also worth while to compare the preceding results with the investigations of the Raman spectra and of the infrared absorption spectra of these compounds.

On the Raman spectra of halogen alkyls and alcohols, many works are listed in the extensive monograph on Smekal-Raman effect of Kohlrausch.[8] Harkins and Bowers[9] have recently investigated particular sequence of compounds with a view to determine the variation of characteristics of the C−halogen bond as the length and structure of the hydrocarbon chain are varied. The final conclusions deduced from the results are briefly summarized as follows:

Table III.

Molecules	Force const. C−X (×10⁵ dynes)	Molecules	Force const. C−X (×10⁵ dynes)	Molecules	Raman lines $\Delta\nu$ (cm^{-1})
CH_3Cl	3.136	CH_3Br	2.61	CH_3OH	1225
CH_3Br	2.695	CH_2Br_2	2.56	C_2H_5OH	1272
CH_3I	2.246	$CHBr_3$	1.82	n-C_3H_7OH	1282
—	—	CBr_4	1.41	n-C_4H_9OH	1286
CH_2Cl	3.12	—	—	iso-C_4H_9OH	1264
CH_2Cl_2	2.94	$SiCl_4$	2.42	sec-C_4H_9OH	—
$CHCl_3$	2.47	$TiCl_4$	2.20	tert-C_4H_9OH	1202
CCl_4	2.00	SnCl	2.00		

(1) As is shown in Table III, the force constant characteristic of the C−halogen bond decreases from chloride to bromide to iodide, in somewhat the same way as the corresponding energies of dissociation.

(2) The force constant characteristic of the C−halogen bond decreases regularly with additional substitutions of halogen atoms for hydrogen atom. A few examples are listed in Table III.

(3) The force constant of the bond either remains constant or else increases only slightly with an increase in length and mass of the normal hydrocarbon chain.

According to Venkateswaran and Bhagavantan[10] the alcohols have three well-defined frequencies common to all of them having values of about 1050, 1250 and 1360 (cm^{-1}). These are attributed to the C−OH group. Interesting variations may be noticed on an examination of these frequencies. The magnitude, as well as the intensity, of the one at 1200 (cm^{-1}) increases as we go up the series of normal alcohols. On the contrary, in the case of the isomers, it is less prominent and assumes a lower value than in the corresponding normal alcohols. These conclusions are in fairly good agreement with the preceding results obtained from the absorption spectra. For tetrachlorides of C, Si, Ti and Sn, and other miscellaneous compounds, there is also a close similarity.

[8] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (1932), p. 146, etc.

[9] W. D. Harkins and H. E. Bowers, Phys. Rev. **38**, 1845 (1928); J. Am. Chem. Soc. **53**, 2425 (1931).

[10] S. Venkateswaran and S. Bhagavantan, Ind. J. Phys. **5**, 129 (1930).

It is also important to notice the results of the infrared absorption spectra of these compounds. But unfortunately, so far as we know, comparatively little work has been done with regard to the halogen alkyls. Easley, Fenner and Spence[11] have investigated the infrared absorption spectra of the halogen derivatives of methane. Ellis has investigated CH_3I, CH_2I_2, CH_2Br_2, $CHBr_3$ and $CHCl_3$. Series attributed to C−Cl, C−Br and C−I oscillations were found, starting at 16.8μ, 17.2μ and 17.5μ, respectively. Bennett and Meyer[12] have investigated the methyl halides CH_3F, CH_3Cl, CH_3Br and CH_3I. Seven bands were found for each of the four compounds. The series converge toward the known bands of methane with a decrease in the atomic weight of the halogen in the halide. In passing from compound to compound the doublet separations increase with a decrease in the atomic weight of the halogen in the halide.

[11] M. A. Easley, L. Fenner and B. J. Spence, Astrophys. J. **67**, 185 (1928).
[12] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

It is also interesting to compare the preceding results with the fact that the larger the value of n the greater the heat of formation of the link C−X in $C_nH_{2n+1}X$. As examples, the values for the alkyl halides and alcohols are given in Table IV.[13] The rise in the heat of formation is

TABLE IV.

MOLECULES	—HEATS OF FORMATION (kcal./mole)— C−O	C−Cl	C−Br
CH_3X	75.9	74.7	61.5
C_2H_5X	76.8	77.6	64.5
n-C_3H_7X	79.2	79.3	66.8
n-C_4H_9X	80.1	—	
iso-C_4H_9X	81.0	81.5	
n-$C_5H_{11}X$	83.1		

about 1 to 2 kcal. per carbon atom added. Various explanations may be given of this, but none is offered as a final solution of the problem.

In conclusion, the author wishes to express his thanks to Professor Y. Takahashi for his helpful criticisms throughout the work, and also to "The Saito Gratitude Foundation" for defraying a part of expenses of the research.

[13] N. V. Sidgwick, *The Covalent Link in Chemistry* (1933), 115.

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Thermodynamic Properties of Sulfur Compounds

I. Hydrogen Sulfide, Diatomic Sulfur and the Dissociation of Hydrogen Sulfide

PAUL C. CROSS,* *Gates Chemical Laboratory, California Institute of Technology*

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The thermodynamic properties of H_2S are calculated from the structure recently obtained by the analysis of an infrared band. $-[(F^0-E_0^0)/T]^*_{298.1}=41.174$. $S^*_{298.1}=49.151$. (Not including the spin contribution.) Montgomery and Kassel's calculations for S_2 are corrected in accordance with Badger's new interpretation of the data of Naudé and Christy. $-[(F^0-E_0^0)/T]_{298.1}=47.242$. $S^0_{298.1}=54.417$. The results are applied to the reaction $H_2S=H_2+\frac{1}{2}S_2$. The energy of dissociation of H_2S into normal atoms, E_0^0, is found to be 173.8 kg cal. per mole.

I. HYDROGEN SULFIDE

THE procedures of calculating thermodynamic properties from spectroscopic data are amply discussed in the literature.[1, 2, 3] The moments of inertia of the H_2S molecule, 2.667, 3.076, 5.845×10^{-40} g cm^2, have recently been obtained from the analysis of a vibration-rotation band in the photographic infrared.[4, 5] The vibrational spectrum has not been sufficiently studied to enable an exact determination of the vibrational constants. For the following calculations the values $\nu_\delta=1260$ cm^{-1} and $\nu_\pi=\nu_\sigma=2620$ cm^{-1}

* National Research Fellow.
[1] W. F. Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).
[2] L. S. Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).
[3] A. R. Gordon and C. Barnes, J. Chem. Phys. **1**, 297 (1933).
[4] P. C. Cross, Phys. Rev. **46**, 536 (1934).
[5] P. C. Cross, Phys. Rev. **47**, 7 (1935).

were used. Since the calculations were not extended to extremely high temperatures, only negligible errors were introduced by using these approximate frequencies and treating the molecules as harmonic oscillators. The tables of Gordon and Barnes[3] greatly facilitated the determination of the vibrational contribution to the free energy, entropy, and heat capacity functions.

From the above moments of inertia, including the symmetry correction, R ln 2, one obtains the following equation for the virtual free energy function of H_2S:[6]

$$[(F^0-E_0^0)/T]^*=4.112-18.300\log_{10}T+[(F^0-E_0^0)/T]_{\text{vib.}}.$$

$$[(F^0-E_0^0)/T](\text{Absolute})=[(F^0-E_0^0)/T]^*+[(F^0-E_0^0)/T]_{\text{spin}}=[(F^0-E_0^0)/T]^*-2.754.$$

Similarly, $S^*=3.836+18.300\log_{10}T+S_{\text{vib.}}$,

$$S(\text{Absolute})=S^*+S_{\text{spin}}=S^*+2.754.$$

The molar heat capacity is equal to $4R$ plus the vibrational heat capacity for temperatures above the boiling point, 212.77°K.[7]

Calculations by direct summation at the temperature 212.77°K agree within the uncertainty in the constants R and k with the values from the approximate equations. The calculations were discontinued above 1800° because of the growing importance of the errors due to incomplete data on the vibrational terms and the lack of useful applications at those temperatures.

TABLE I. *Free energy, entropy, and heat capacity of H_2S.* (Not including the spin contribution.)

T	$-[(F^0-E_0^0)/T]^*$	S^*	C_p	T	$-[(F^0-E_0^0)/T]^*$	S^*	C_p
212.77	38.489	46.441	7.978	1000	51.24	60.25	10.85
298.1	41.174	49.151	8.121	1100	52.11	61.30	11.17
400	43.53	51.58	8.43	1200	52.92	62.29	11.46
500	45.34	53.50	8.81	1300	53.67	63.22	11.72
600	46.83	55.14	9.23	1400	54.39	64.09	11.94
700	48.13	56.60	9.67	1500	55.06	64.92	12.13
800	49.27	57.92	10.09	1600	55.70	65.71	12.30
900	50.30	59.13	10.49	1700	56.31	66.46	12.45
				1800	56.90	67.17	12.58

[6] $R=1.9869$ (Int. Crit. Tab.).
[7] W. F. Giauque, private communication.

II. Diatomic Sulfur

Badger's[8] reinterpretation of the data of Naudé and Christy[9, 10] on the S_2 band spectrum gives the S−S separation as 1.84A in place of the former value of 1.60A which was in serious disagreement with all empirical methods of estimating interatomic distances.[11] The new values of $-(F^0-E_0^0)/T$ may be obtained by adding 0.55 to those given by Montgomery and Kassel.[12] $-[(F^0-E_0^0)/T]_{298.1}=47.242$. $S^0_{298.1}=54.417$.

III. Dissociation of Hydrogen Sulfide

Applying the results reported here with Giauque's[13] calculations on hydrogen to the equilibrium measurements discussed by Lewis and Randall,[14] one obtains the value of ΔE_0^0 for the reaction $H_2S(g)=H_2(g)+\frac{1}{2}S_2(g)$, $\Delta E_0^0=19.62\pm0.03$ kg cal. The small probable error illustrates the accuracy of the agreement between the experimental and calculated free energies. Since the energies of dissociation into normal atoms are known for H_2[15] and S_2[10], the energy of dissociation of H_2S into normal atoms can be calculated $E_0^0(H_2S)=E_0^0(H_2)+\frac{1}{2}E_0^0(S_2)-\Delta E_0^0=-102.9-51.3-19.6=-173.8$ kg cal. per mole. This corresponds to −86.9 kg cal. per H−S bond.

I wish to thank Professor R. M. Badger for access to his analysis of the S_2 spectrum before publication and for his interest in these results.

[8] R. M. Badger, Phys. Rev. **46**, 1025 (1934).
[9] S. M. Naudé and A. Christy, Phys. Rev. **37**, 490 (1931).
[10] A. Christy and S. M. Naudé, Phys. Rev. **37**, 903 (1931).
[11] The sum of the double bond radii gives 1.88A (L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932)). The relation between the force constant and interatomic distance gives 1.90A (R. M. Badger, J. Chem. Phys. **2**, 128 (1934)).
[12] C. W. Montgomery and L. S. Kassel, J. Chem. Phys. **2**, 417 (1934).
[13] W. F. Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).
[14] Lewis and Randall, *Thermodynamics*, p. 541, McGraw Hill, New York, 1923.
[15] Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 269, Cambridge, 1932.

The Acidities of Ketones and the Mechanism of Prototropic Change

H. B. WATSON, W. S. NATHAN AND L. L. LAURIE, *Department of Chemistry, The Technical College, Cardiff, Wales*

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The observation of acidity in the brominated acetones is attributed to coordination of carbonyl carbon and hydroxyl ion, the process being preceded by electromeric change to the semipolar form. Acid- and base-catalyzed prototropy is regarded as involving a similar electromeric change, brought about by interaction with the catalyst, and followed by transformation of the semipolar form either to ketone or to enolic ion. The measured velocity will thus be dependent upon (a) the rate of reaction of ketone and catalyst, and (b) the proportion of the semipolar form which changes to enol. The application of this view, in conjunction with the conception of quantum-mechanical resonance as developed by Pauling, renders possible the satisfactory interpretation of a number of observations relating to the prototropic changes of carbonyl compounds.

IT was observed some three years ago[1] that the substitution of halogen atoms in the acetone molecule confers upon the ketone acidic characters which become progressively stronger as the number of substituent atoms is increased. Thus the *pH* values of $M/400$ aqueous solutions of various brominated acetones were found to be as follows:

monobromoacetone	5.4
as-dibromoacetone	4.7
s-dibromoacetone	4.3
$\alpha\alpha\alpha$-tribromoacetone	3.8
as-tetrabromoacetone	2.8.

None of the ketones gave an instantaneous reaction with bromine, the absence of any detectable quantity of enolide thus being indicated. It was evident, therefore, that the acidity is associated with the ketonic form, and ionization of α-hydrogen was postulated, notwithstanding the fact that the acidity developed slowly, some hours being required for the attainment of the final maximum values recorded above. We wish now to suggest an alternative interpretation which, we feel, is more in harmony with the general reactions of carbonyl compounds, and particularly with our recent observation that benzophenone (in which there is no α-hydrogen) also has a definite though small acidity.

Numerous investigations have demonstrated the capacity of the carbonyl group to coordinate both with protons and with anions, and it is evident that processes such as cyanohydrin formation (where the anion adds first[2]) and the alkaline hydrolysis of esters (involving addition of hydroxyl[3]) must be accompanied by the transfer of a pair of electrons from the double bond to the sole control of the oxygen atom.[4] Indeed, both the reactivity of the carbonyl group and the ketonic ultraviolet absorption band have been ascribed by Lowry[5] to "polar activation" in which electrons are "displaced from carbon towards oxygen, a process which (if continued far enough) would culminate in the ionization of one link of the bond, and the conversion of the nonpolar into a semipolar double bond, as indicated by the scheme $\rangle C=O \rightleftarrows \rangle \overset{+}{C}-\overset{-}{O}$," while Pauling and Sherman[6] have recently suggested that the unusually high energy of formation of the carbonyl group is due to quantum-mechanical resonance between the normal and semipolar structures. The "decreased rigidity" of the carbon-nitrogen double bond in oximes, brought about by interaction with an ion-pair,[7] may be due to an electromeric change of a similar type, while the same process may be supposed to occur in the production of aldols, hydrazones, oximes, pinacols and metal ketyls, and to be responsible for the colors of solutions of aldehydes and ketones in concentrated sulphuric acid.[8]

[1] Watson and Yates, J. Chem. Soc. (1932), 1207.

[2] Lapworth, J. Chem. Soc. **83**, 995 (1903); **85**, 1206 (1904).

[3] Lowry, J. Chem. Soc. **127**, 1379 (1925). Ingold and Ingold, ibid. (1932), 756.

[4] Compare Robinson, *Outline of an Electrochemical (electronic) Theory of the Course of Organic Reactions*, Institute of Chemistry, London, 1932, p. 16.

[5] Lowry, J. Chem. Soc. **123**, 822 (1923); (1926), 620.

[6] Pauling and Sherman, J. Chem. Phys. **1**, 606 (1933).

[7] Taylor and Roberts, J. Chem. Soc. (1933), 1439.

[8] Baker, J. Chem. Soc. (1931), 307. Compare Pfeiffer's conception of "one-sided saturation," Ann. **404**, 1 (1914); **412**, 253 (1916).

In the light of these considerations, the acidity of the brominated acetones is probably to be attributed to the acceptance of hydroxyl (from water) by the carbon atom of the carbonyl group, conversion of this group to the semipolar form having first occurred;

$$>C=O \rightarrow >\overset{+}{C}-\bar{O} \xrightarrow{H_2O} >C(OH)-\bar{O}+H^+.$$

Because of the strongly dipolar character of the carbon-halogen bond (C→Br) coordination with hydroxyl ion will occur in preference to coordination with proton and will become more facile as the number of halogen atoms increases. This view of the process for which more definite experimental evidence is now being sought, brings it into line with the reactions referred to above (cyanohydrin formation, ester hydrolysis) in which the controlling stage is the addition of the anion.

The same conceptions may be employed in the consideration of the prototropic changes of ketones and other carbonyl compounds. The kinetics of these changes are conveniently studied by measurement of velocities of bromination, as first pointed out by Lapworth.[9] It is universally recognized that the prototropy may proceed via either of two routes, and the series of changes by which the acid and base-catalyzed reactions are usually represented are identical in their essentials with those postulated over thirty years ago by Lapworth and Hann,[10] the first step being either the addition of proton to carbonyl oxygen (acid catalysis),

$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}=O \xrightarrow{H^+} -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}=OH^+ \xrightarrow{-H^+} -\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}-OH,$$

or the removal of proton from α-carbon (basic catalysis),

$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}=O \xrightarrow{-H^+} -\underset{|}{\overset{|}{\bar{C}}}-\underset{|}{\overset{|}{C}}=O \rightarrow -\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}-\bar{O} \xrightarrow{H^+} -\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}-OH.$$

Since, however, the carbonyl group is capable, under appropriate conditions, of forming addition products with ions of *either* sign, and more particularly in view of the considerations outlined above, we wish to suggest that the attack of catalysts of *both* types consists in the initial formation of such a complex. The ketone-catalyst bond is frequently, no doubt, merely a transient one, but it nevertheless provides an efficient means for the communication of energy to a definite point in the molecule. As Hinshelwood points out[11] in connection with the catalytic decomposition of ethers by iodine, "the catalyst brings the energy into that part of the molecule where it can be usefully employed in promoting chemical transformation." The energy thus communicated to the carbonyl group will bring about activation of the double bond by an electromeric change (not necessarily complete) as visualized by Lowry. The semipolar form, however, will be immediately transformed to a more stable structure, either (1) by regenerating the original ketonic form (reversal of the primary electromeric change) or (2) by production of the enolic ion.

$$-\underset{|}{\overset{|}{C}}-\overset{+}{\underset{|}{\overset{|}{C}}}-\bar{O} \rightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}=O, \qquad (1)$$

$$-\underset{|}{\overset{|}{C}}-\overset{+}{\underset{|}{\overset{|}{C}}}-\bar{O} \rightarrow -\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}-\bar{O}. \qquad (2)$$

Mechanism (2) recalls the photochemical decomposition of keten,[12] where energy is absorbed by the carbonyl group and transferred to the adjacent olefinic bond with rupture of the latter.

In the case of any particular ketone under given conditions, a definite proportion of the semipolar form will undergo transformation (2). The ejection of a proton presents no difficulty in the case of reactions in water or acetic acid medium (such as have been investigated in these laboratories during the past few years), for the ketone is surrounded by acceptor molecules which will effect its removal immediately the

[9] Lapworth, J. Chem. Soc. **85**, 30 (1904). For summary of literature up to 1930, see Watson, Chem. Rev. **7**, 173 (1930).

[10] Lapworth and Hann, J. Chem. Soc. **81**, 1512 (1902). For more recent statements of these mechanisms, see Lowry, J. Chem. Soc. (1927), 2557. Watson and Yates, reference 1. Pedersen, J. Phys. Chem. **38**, 581 (1934).

[11] Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford, 1933, p. 229.

[12] Norrish, Crone and Saltmarsh, J. Chem. Soc. (1933), 1533.

internal facilitating process occurs. It is unnecessary, moreover, to postulate the formation of the enol itself in all bromination processes, for the enolic ion doubtless reacts instantaneously with halogen.

An advantage that may be claimed for the view here presented is the similarity between the acid and basic mechanisms, which is obvious when they are represented as follows:

$$-\overset{|}{\underset{|}{CH}}-\overset{|}{\underset{|}{C}}=O + H^+ \rightleftarrows -\overset{|}{\underset{|}{CH}}-\overset{|}{\overset{+}{\underset{|}{C}}}-\bar{O}(H^+)$$

$$\rightarrow H^+ + -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\bar{O}(H^+),$$

$$-\overset{|}{\underset{|}{CH}}-\overset{|}{\underset{|}{C}}=O + A^- \rightleftarrows -\overset{|}{\underset{|}{CH}}-\overset{|}{\overset{+}{\underset{|}{C}}}(A^-)-\bar{O}$$

$$\rightarrow H^+ + -\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\bar{O} + A^-.$$

Assuming these mechanisms, the measured velocity of prototropic change (rate of bromination) will depend upon two factors, *viz.*, (A) the rate of reaction of the ketone with the catalyst, and (B) the proportion of the semipolar form which is transformed to the enolic ion. The application of these views, in conjunction with the conception of quantum-mechanical resonance as developed by Pauling, provides a very satisfactory interpretation of numerous observations relating to the prototropy of carbonyl compounds.

The Prototropy of Nuclear-Substituted Acetophenones

In a series of *very similar compounds* undergoing change with *identical conditions* of temperature, medium, and catalyst concentration, it may probably be assumed that the second factor, *viz.*, the proportion of semipolar form becoming enol ion, will not vary appreciably. Further, Bradfield and his collaborators[13] have observed that the differences in the velocities of chlorination of a series of phenolic ethers of the general formula $X.C_6H_4.OR$ are due solely to different energies of activation,* and it is reasonable to suppose that the same will apply to the prototropy of a series of compounds such as the *p*-substituted acetophenones.[14] In the acid-catalyzed reaction, the presence of an electron-attracting substituent will render less facile the approach of the positive ion, additional work being performed by the approaching ion against the superimposed field due to the substituent, and the reverse will, of course, hold for an electron-repelling group. The result will be an increase or decrease in the energy of activation, and, in fact, when the kinetic equation is applied in its simplest form (velocity = collision number $\times e^{-E/RT}$), an accurate relationship is found[14] between the differences in the energies of activation for the prototropy of $X.C_6H_4.CO.CH_3$ and $C_6H_5.CO.CH_3$ (calculated from the relative velocities of bromination) and the dipole moments of C_6H_5X, the relevant expression being $E-E_0=-C(\mu-a\mu^2)$. An attempt is now being made to obtain direct experimental proof of the postulate that, in the system here considered, substituents affect only (or at any rate principally) the energy of activation. It may also be noted that Hammett and Pfluger[15] have recently found a quantitative relationship between the velocities of reaction of substituted benzoic esters with trimethylamine and the dissociation constants of the corresponding benzoic acids.

The Prototropy of Halogenated Acetones

Parallel with the increasing acidity which accompanies the introduction of halogen atoms into the acetone molecule (referred to in the opening paragraph of this paper), there is a decrease in the effectiveness of acids as catalysts of the prototropic changes of these compounds, and a similar increase in the effectiveness of basic catalysts.[1] Thus, employing 0.1M ketone solutions in 50 percent acetic acid, the point at which the velocity of prototropy of acetone has

[13] Bradfield and Jones, J. Chem. Soc. (1928), 1106, 3073; (1929), 2810; (1931), 2903. Bradfield, Jones and Spencer, ibid. (1931), 2907. Bradfield, Chemistry and Industry **51**, 254 (1932).

* Since the preparation of this paper, Williams and Hinshelwood (J. Chem. Soc. (1934), 1079) have observed that the influence of substituents upon the velocity of benzoylation of aromatic amines depends principally upon changes in activation energy.

[14] Nathan and Watson, J. Chem. Soc. (1933), 890.

[15] Hammett and Pfluger, J. Am. Chem. Soc. **55**, 4079 (1933).

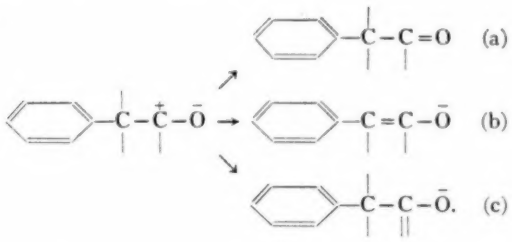
its minimum value[16] is not detectable, while, in order to reach this point for monobromo-, *as*-dibromo-, and *s*-dibromoacetones, the addition of hydrochloric acid at concentrations of 0.002, 0.2 and 0.45M, respectively, is necessary, and the prototropic changes of *ααα*-tribromo- and *as*-tetrabromo-acetones occur via the basic mechanism even in presence of 2M hydrochloric acid. The influence of the powerfully electron-attractive halogen atoms upon the reaction of ketone with catalyst is sufficient to explain these observations, for it will oppose the approach of hydrogen ion and facilitate the approach of an anion. Probably then, this is again the main factor involved.

The Prototropy of the Phenylacetones

A very different position is here revealed. The velocities of prototropic change of mono- and *s*-diphenylacetones* for 0.1M solutions in 75 percent acetic actid at 25°, we find, are as follows, the figures referring to fall of $N/50$ titre per minute for 20 cc of reaction mixture;

Ketone	Velocity		
	HCl = 0	HCl = 0.0095M	HCl = 0.476M
acetone	0.013	0.109	0.675
monophenylacetone	0.016	0.227	1.390
s-diphenylacetone	0.007	0.076	0.625
(acetophenone)	—	—	0.243

The relative strengths of phenylacetic and acetic acids ($K = 4.88\times10^{-5}$ and 1.76×10^{-5}, respectively[17]) indicate that, relatively to hydrogen, phenyl is a weakly electron-attracting group, as pointed out by G. N. Lewis[18] and by Ashworth and Burkhardt.[19] Its presence will therefore be unfavorable to coordination with an acid catalyst, and the rates of reaction of the ketones referred to in the table will no doubt be in the descending order acetone > monophenylacetone > diphenylacetone > acetophenone (in the last-named, phenyl is attached directly to carbonyl, and hence will exert a relatively large effect). This is not, however, the order of the measured velocities, and, if the views outlined above be correct, there must be considerable variation in the proportion of semipolar form which is transformed to enol. In the case of monophenylacetone, the rearrangement of this form may give rise to three distinct entities, the ketonic and two enolic forms;



The product isolated after bromination of this ketone is $C_6H_5.CHBr.CO.CH_3$,[20] and it is thus shown experimentally that, of the two enols, the favored form is (b). It is evident, too, that the stability of (b), which contains a long system of alternate single and double bonds, will be considerably enhanced by resonance.* Pauling and Sherman[6] calculate the value 1.71 v.e. for the resonance energy of phenyl between the five possible structures, and find that the additional double bond in phenylethylene contributes a further 0.29 v.e. There is good reason to suppose, therefore, that, in the case of monophenyl-

[16] Compare Dawson and Dean, J. Chem. Soc. (1926), 2872.

* Dawson and Ark (J. Chem. Soc. **99**, 1742 (1911)), by measurement of velocities of iodination, found that phenylacetone undergoes prototropic change much more rapidly than does acetone, but they failed to obtain satisfactory results for *s*-diphenylacetone. We experienced great difficulty in preparing pure specimens of these ketones from the appropriate calcium salts. An instantaneous bromine absorption was ultimately removed from monophenylacetone by two treatments with 5 percent of bromine in carbon tetrachloride, followed by vacuum distillation. The pure ketone has b.p. 87°/4 mm. *s*-diphenylacetone was obtained pure (b.p. 154°/5 mm, m.p. 33.9°, compare Young, J. Chem. Soc. **59**, 623 (1891)), by very carefully regulated heating of calcium phenylacetate followed by crystallization from carbon tetrachloride or petroleumether. We found later that the impurities can be removed by steam, the residue giving a pure product on crystallization. Samples of both ketones deteriorate on keeping, particularly if light and air are admitted.

[17] Jeffery and Vogel, J. Chem. Soc. (1933), 1637; (1934), 166. Dippy and Williams, ibid. (1934), 161.

[18] Lewis, *Valence and the Structure of Atoms and Molecules* (1923), p. 150.

[19] Ashworth and Burkhardt, J. Chem. Soc. (1928), 1793. Compare Nathan and Watson, ibid. (1933), 217.

[20] Kolb, Ann. **291**, 267 (1896).

* "The tendency of two or more double bonds to arrange themselves alternately with single bonds" is referred to by Lapworth and Manske (J. Chem. Soc. (1928), 2535), who note that "such an arrangement is ordinarily associated with an element of stability." In this "Thiele factor" they find (ibid. (1930), 1976) an interpretation of the low stability of the cyanohydrins of ketones where phenyl is in direct attachment to carbonyl. Compare Linstead, ibid. (1929), 2501; Watson and Yates, reference 23.

acetone, a relatively high proportion of the semipolar form will be transformed to the enol (b), and this suffices to explain the high value of the measured velocity of prototropic change. The velocity is thus influenced by two opposing factors (depression of the speed of reaction with the catalyst, and increase in the proportion of semipolar form changing to enol), and in *s*-diphenylacetone, where the electron-attractive characters of *two* phenyl groups oppose reaction with the acid catalyst, these factors approximately balance each other, the resulting speed being not very different from that observed in the case of acetone itself. Preliminary experiments upon the prototropy of monobenzylacetone have indicated that this compound also changes at about the same rate as acetone, both effects being practically eliminated by the intervening methylene group.

A discussion, on similar lines, of the prototropy of the carbethoxyacetones (acetoacetic and acetone-dicarbocylic esters) is contemplated, but is at present undesirable, owing to the conflicting evidence regarding the effect of acid catalysts.[21]

Saturated Aliphatic Acids

Pauling and Sherman[6] find that the carboxyl group has a resonance energy of 1.2 v.e. because of the complete degeneracy between two equivalent forms (as expressed by the Hantzsch formula). The absence of carbonyl properties is thus readily accounted for, and it also becomes evident that the enolic form, in which this group is destroyed, will be relatively unstable, and hence produced in negligible quantity from the semipolar form (if, indeed, the last-named ever exists). One of us has shown, indeed,[22] that the halogenation of acetic acid and its homologs is not preceded by prototropic change. In an acyl halide (e.g., acetyl bromide) the dipolar character of the bond linking halogen with carbonyl carbon will doubtless prevent any appreciable reaction with an acid catalyst, while the properties of the compound preclude prototropy by the basic mechanism. Neither the saturated monocarboxylic acids nor their halides, therefore, undergo prototropic change, so far as can be detected, and the fact that acyl halides can be directly halogenated at the α-carbon atom must be ascribed to some additional property of the halogen, not necessarily connected with the dipolar nature of the carbon-halogen bond.[23] Malonic acid, however, is known to undergo prototropic change with relative ease, while succinic acid may perhaps react with halogens in its enolic form.[24] In both cases the enol retains the stability due to *one* carboxyl group, and in the former, additional stability is gained[25] by resonance between the structures O=C−C=C−O and O−C=C−C=O.

[21] K. H. Meyer, Ann. **380**, 212 (1911). Watson and Yates, J. Chem. Soc. (1933), 220. Pedersen, J. Phys. Chem. **37**, 751 (1933).

[22] Watson, J. Chem. Soc. **127**, 2067 (1925). Compare Chem. Rev., reference 9.

[23] Compare Watson and Yates, reference 21.

[24] Hughes and Watson, J. Chem. Soc. (1930), 1733.

[25] Compare Wheland, J. Chem. Phys. **1**, 731 (1933).

Studies with Vibrating Mechanical Models

I. Benzene, Toluene and the Phenyl Halides

D. E. TEETS AND D. H. ANDREWS, *Johns Hopkins University, Department of Chemistry*

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By continuing the work of Kettering, Shutts and Andrews, mechanical models have been constructed for the series of compounds:

C_6H_6, $C_6H_5CH_3$, C_6H_5Cl, C_6H_5Br, C_6H_5I.

The mechanical frequencies of the simpler types of motion show some correlation with the spectral lines, especially in the shifts of frequency in passing down the series of compounds. The types of motion observed are in fair accord with the types deduced with the aid of group theory.

KETTERING, Shutts and Andrews,[1] in their initial study of vibrating mechanical models of molecules, showed that it was possible to construct models of benzene and toluene in which the shifts of frequency caused by the introduction of the substituent group closely resembled the corresponding shifts in the spectral lines. In order to make a more extensive study of this type of shift we have constructed models of benzene, toluene, chlorobenzene, brombenzene and iodobenzene, and have observed their mechanical spectra.

In details of construction these models are similar to the previous ones,[1] the exact dimensions being given in Table I. A photograph of

TABLE I.

Spring type	1	2
Bond	C−H	C−C
Spring wire diameter	11/64	11/64 in.
Outside diameter spring coil	4.5	5 cm
Number of active turns	5	5
Distance between ball centers	11.4	16 cm
Weight of spring	81	90 g
Ratio of stretching to bending constant	5	11.4
Atom represented:	C	H
Weight of ball:	869	76 g

the model of toluene is shown in Fig. 1. The atoms were represented by balls with masses approximately in the ratios of the atomic weights. The bonds were represented by two types of spring, type No. 1 being used for the carbon-hydrogen bonds and type No. 2 for the carbon-carbon and carbon-halogen bonds. The spring constants were based on data obtained from methane and ethane.

The model representing the benzene nucleus was made with single-bond springs joining neighboring atoms in the ring, and two single-bond springs in series joining atoms para to each other.

The procedure followed was in general the same as that described in the earlier paper, the principal difference being in the type of stroboscope used, which consisted of a bright lamp placed behind a rotating disk with holes around the rim through which a beam of light passed to the model. The rotating disk was driven by a variable speed motor.

The types of motion observed are shown in Fig. 2. The drawings reproduce as closely as possible the original sketches noted when the motions were observed for the first time. In many cases these observations are somewhat inaccurate as may be surmised by comparison with the types of motion deduced from group theory which are discussed later.

The r.p.m. at which the modes of motion were excited are given in Table II and plotted in Figs. 3 and 5. In Figs. 4 and 5 there are shown plots of the Raman spectra of benzene,[2] toluene,[3] and the phenyl halides[4] compiled from various sources.

In order to make a comparison of the nu-

[1] C. F. Kettering, L. W. Shutts and D. H. Andrews, Phys. Rev. **36**, 531 (1930).

[2] Krishnamurti, Ind. J. Phys. **6**, 543 (1931); R. W. Wood, Phys. Rev. **36**, 1431 (1930); K. W. F. Kohlrausch, Monatshefte **52**, 376 (1929); P. Grassman and J. Weiler, Zeits. f. Physik **86**, 321 (1933).

[3] K. W. F. Kohlrausch, *Der Smekal Raman Effekt*, Julius Springer, Berlin (1931).

[4] J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933); **2**, 120 (1934).

TABLE II. *Model frequencies.*

	C_6H_6	$C_6H_5CH_3$	C_6H_5Cl	C_6H_5Br	C_6H_5I	
X		190	200	180	166	r.p.m.
W		200	200	180	166	
		300	300*	340	340	A_1
A	340					
		340	360*	360	360	A_2
Y		440	390	300	230	
C	510	480	480	480	500	
D_1	610					
D_2	610					
E_1		600	540	580	510	
F	680					
E_2		600				
E_5		600	610	600		
E_6		620	620	610	610	
		700	700	700	700	G_1
G	790					
		740	780	740	780	G_2
E_3		810	740	880	880	
H	880	880	900	900	900	
		990	940	920	1060	I_1

	C_6H_6	$C_6H_5CH_3$	C_6H_5Cl	C_6H_5Br	C_6H_5I	
I	1040					
				1060		I_2
		960	920	960	960	J_1
J	960					
		1000	1000	1000	1010	J_2
E_7			1100	1100	1100	
E_3	980					
E_4		1100				
K	1160					
L	1180					
M	1280	1400	1480	1400	1380	
N	1300	1200	1280	1280	1280	
O	1380	1280	1300	1300	1300	
P	1390					
Q	2060	2060	2060	2060	2060	
R	2120	2120	2120	2100	2120	
V	2080					
S	2200	2200	2200	2180	2160	

* Identification of the type of motion not certain.

merical values somewhat easier a scale of wave numbers has been added in Fig. 3 so placed that the value of 992 cm^{-1} falls at the line for the *H* motion in benzene. As will be shown in the following paper, there is considerable evidence that this strong line in benzene corresponds to the *H* type of motion.

Figs. 3 and 4 show certain apparent correlations between the mechanical frequencies and the Raman spectra. The *X-W* motions in the phenyl halide models agree quite well in position and relative shift with the series of lines lying at the extreme lower limit of the Raman spectra. The corresponding motion in toluene lies somewhat lower than the Raman line apparently associated with it. This appears to be due to the weight of the three springs representing the carbon-hydrogen bonds of the CH_2 group, which makes the total weight of the CH_3 group relatively too great.

There is a correspondence between the positions and shifts of the *Y* type of motion and the series of lines starting at about 500 cm^{-1} in toluene and ending at about 250 cm^{-1} in iodobenzene. The identification of these lines with the motions of the substituent groups is in general accord with the conclusions drawn by Kohlrausch[5] and his associates in their noteworthy series of investigations on the Raman spectra of phenyl derivatives.

There is a superficial resemblance between the series of lines in the Raman spectrum starting with 607 cm^{-1} in benzene and the series in the mechanical spectrum labeled *C*. We believe, however, that this is not a true correlation. As will be shown in the next article of this series there is considerable evidence that the series starting at

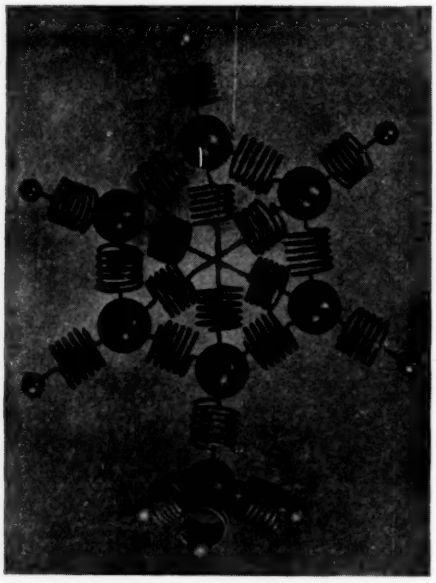

FIG. 1. Model of toluene.

[5] K. W. F. Kohlrausch and A. Pongratz, Sitz. Ber. Akad. Wien [IIb] **142**, 637 (1934).

607 cm^{-1} is due to deformation vibrations in the plane of the ring.

Kohlrausch and Pongratz[2] point out that there is evidence for a series of lines starting with 849 cm^{-1} in benzene. With the exception of the line in C_6H_5Br the series of mechanical vibrations starting with F and ending with E_1 show a close relation to these Raman lines.

The relative shifts of the H motion correspond to the shifts of the series of strong lines in the Raman spectra which start with the 992 cm^{-1} line in benzene. Since the shifts are so small, it is not very positive evidence.

There is another slight resemblance possibly worth noticing, namely, that between the series of mechanical vibration $I-I_1$ and the series of Raman lines starting at 1176 cm^{-1} in benzene and ending at 1062. Kohlrausch and Pongratz include the 1209 cm^{-1} toluene line in this series instead of the 1154 cm^{-1} line.

Fig. 5 shows the mechanical frequencies and Raman spectra for the 3000 cm^{-1} region usually associated with the motions which result primarily in stretching the carbon-hydrogen bond. The scale of wave numbers has been placed so as to make R in C_6H_6 fall at 3063 cm^{-1}. Although there is some evidence in the Raman spectra for three principal series of lines such as are shown by the models, the correlation between the shifts is not particularly good.

It is interesting to compare the types of motion observed in the models with the modes of motion deduced by E. Bright Wilson, Jr.,[6] from group theory as shown in Fig. 2b. In seeking correspondences between the two sets of data several facts must be borne in mind. In the first place, Wilson has not given all his results in the form of complete types of motion. It is necessary to add together certain of his figures in

[6] E. B. Wilson, Jr., Phys. Rev. **45**, 707 (1934).

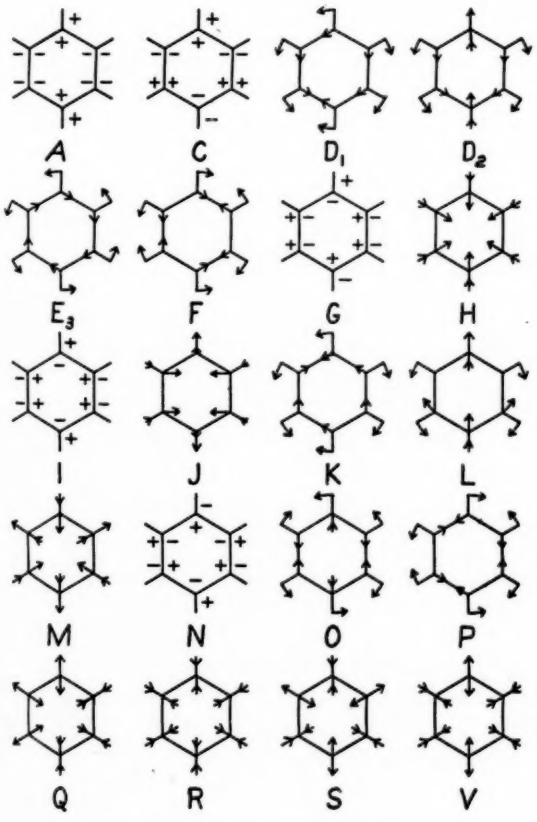

FIG. 2a. Benzene, model motions.

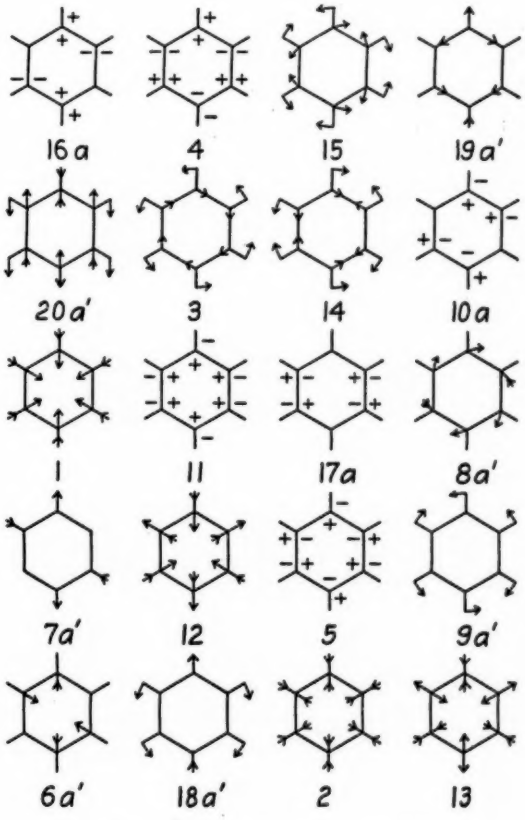

FIG. 2b. Benzene, group theory motions.

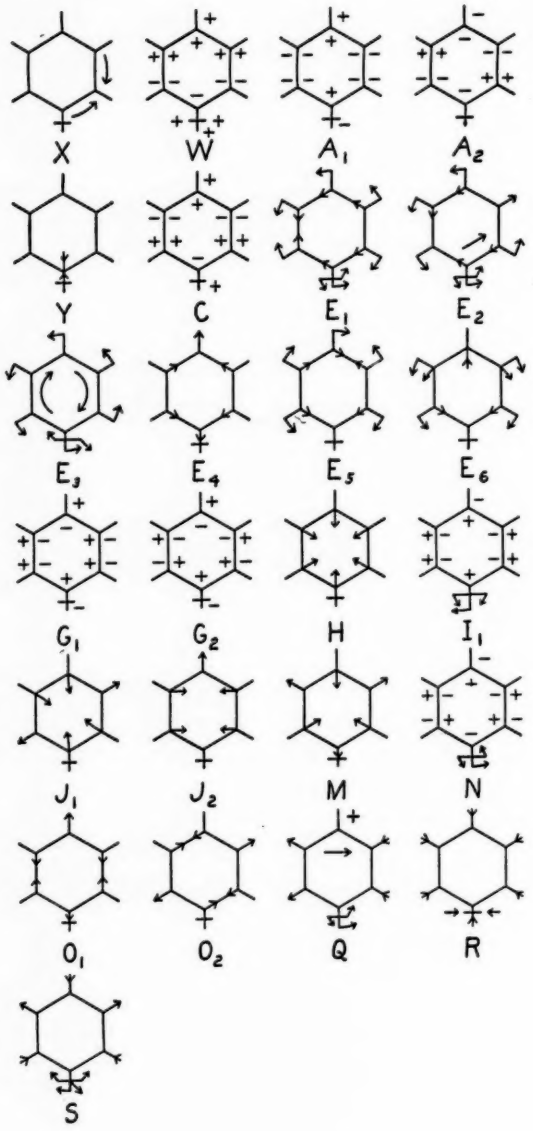

FIG. 2c. Toluene.

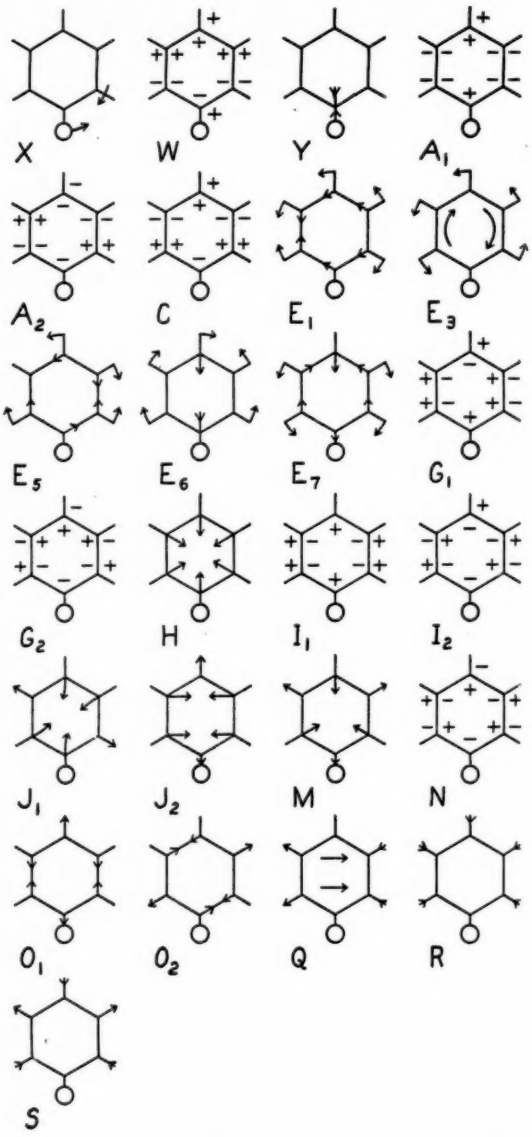

FIG. 2d. Halogen derivatives.

order to obtain the final result which gives the actual manner of vibration. In the second place, Wilson's results are based on the Pauling resonance formula for benzene so that in certain types of motion one would expect differences between his results and the behavior of the centric model. Finally one must remember that the precise direction of motion depends on the relative elasticity of the various bonds with respect to bending and stretching. Since we have almost no information on this point at the present time we may expect considerable deviation in angle between any two methods which attempt to predict these motions.

With these facts in mind, one must conclude that the resemblance between the two sets of motions is quite striking. There are the following exact correspondences: $C=4$, $M=12$, $H=1$, $F=14$, $E_a=3$, $N=5$, $P=15$, $R=2$, $S=13$. By adding together certain of Wilson's incomplete

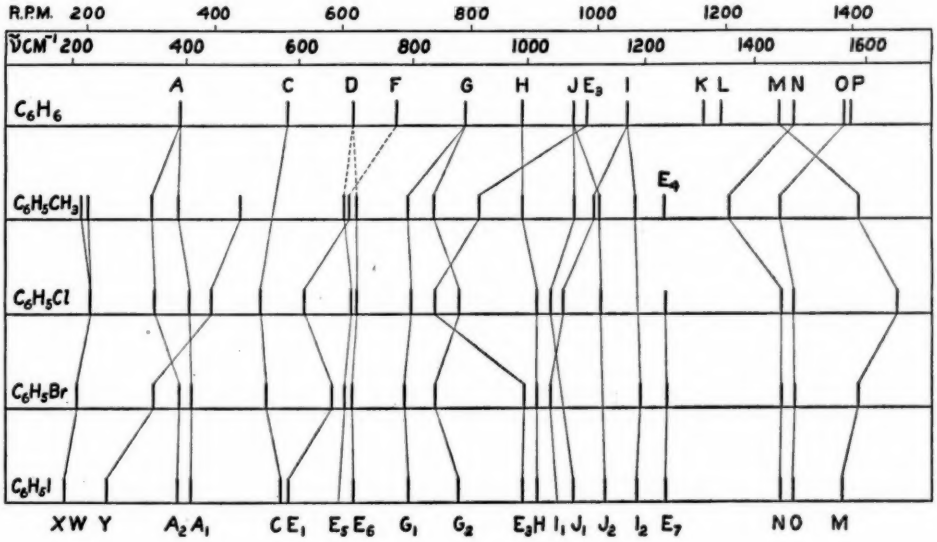

FIG. 3. Model frequencies.

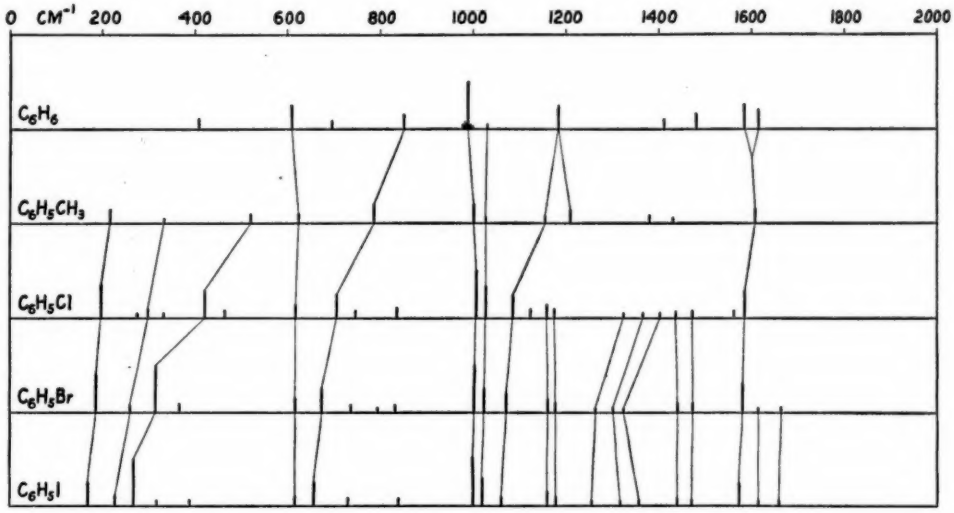

FIG. 4. Raman frequencies.

types of motion one also finds the following correspondences: $A=16_{ar}+16_{al}$; $D_2=18_a+19_a$; $I=17_{ar}+17_{al}$; $J=6_{ar}+6_{al}+7_{ar}+7_{al}$; $V=6_{ar}+6_{al}-7_{ar}-7_{al}$; $G=10_{ar}+10_{al}$. The subscripts r and l refer to right-handed and left-handed types of motion. Finally there are the two correspondences which are incomplete in the part indicated by the asterisk: $L=18_a+19_a$*; $O=9_a+6_a$*. The types of motions D_1, K and Q were not found by Wilson.

It is interesting to remember that, quite apart from any relation which they bear to real molecules, the models are directly related to group theory, since they constitute a vibrating mechanical system which is amenable to treatment by this branch of mathematics. The models thus provide a means of testing the postulates of group theory without passing through the indirect and frequently uncertain medium of spectroscopic analysis.

After the work with these models was completed an attempt was made to study this same

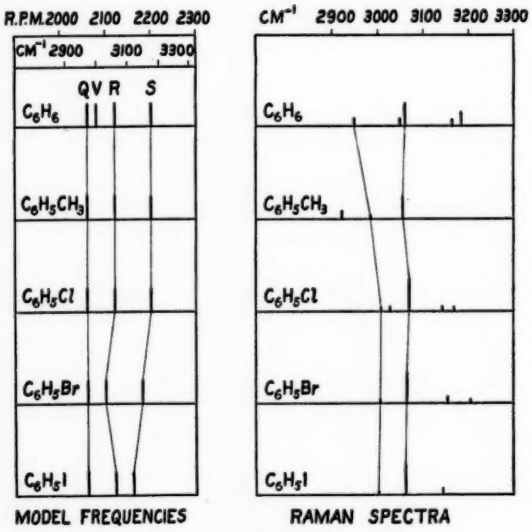

FIG. 5.

series of compounds with two other sets of models in which the springs representing the benzene ring correspond, respectively, to the Kekulé and to the Pauling resonance formulas. The results were quite unsatisfactory. As found in the earlier model studies,[1] it is very difficult to get vibration in a steady state at a sharp resonance frequency if the molecule is what may be called the "floppy" type such as a long hydrocarbon chain. The model of the centric formula was compact enough to avoid this difficulty, the cross bonds acting to stabilize the vibration, but the models representing the Kekulé and Pauling resonance formulas were very unstable and yielded results that appeared to be incomplete and unreliable.

From this we may conclude that the usefulness of the models will be restricted largely to the study of certain relatively simple and stable types of vibration such as the X, Y and H movements where one can expect to get qualitative evidence of the effect of a change of mass on the frequency.

The authors wish to thank Mr. Charles F. Squire for the study which he made of the resonance and Kekulé models in connection with the work reported here.

MARCH, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

Studies with Vibrating Mechanical Models
II. The Series: $C_6H_5Cl-C_6Cl_6$

J. W. MURRAY, V. DEITZ AND D. H. ANDREWS, *Department of Chemistry, The Johns Hopkins University*

(Received September 4, 1934)

Mechanical models have been constructed for the following molecules based on the Pauling resonance formula for benzene: C_6H_6; C_6H_5Cl; *o*-, *m*-, *p*-$C_6H_4Cl_2$; (1, 2, 3)-, (1, 2, 4)-, (1, 3, 5)-$C_6H_3Cl_3$; C_6Cl_6. The mechanical spectra of these models have been observed and compared with the Raman spectra. The shifts in frequency observed in passing down the series are the same in both mechanical and Raman spectra in a number of cases. This makes possible the identification of several of the lines connected with the motions of the chlorine atoms and of the line at 992 cm^{-1} associated with the symmetrical expansion of the benzene ring. The types of motion show an evolution from the symmetrical group of C_6H_6, which can be correlated with group theory, through the various doublets and triplets associated with the less symmetrical intermediate compounds, to the group connected with C_6Cl_6 which is similar to that of C_6H_6 except for the inversion of frequency order due to the increased mass of the substituent atoms

IN studying the variation of characteristic frequencies with structure, some of the most interesting shifts in frequencies are those associated with the change in position of substitution in the benzene ring. Since a rather complete series of Raman spectra are available for the various chloro-derivatives of benzene, this group of compounds was selected as the basis for an extension of the work with the vibrating mechanical models.

The atoms and bonds were represented by the same types of ball and spring used in work by Teets and Andrews[1] reported in the previous article of this series. The procedure followed for

[1] D. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).

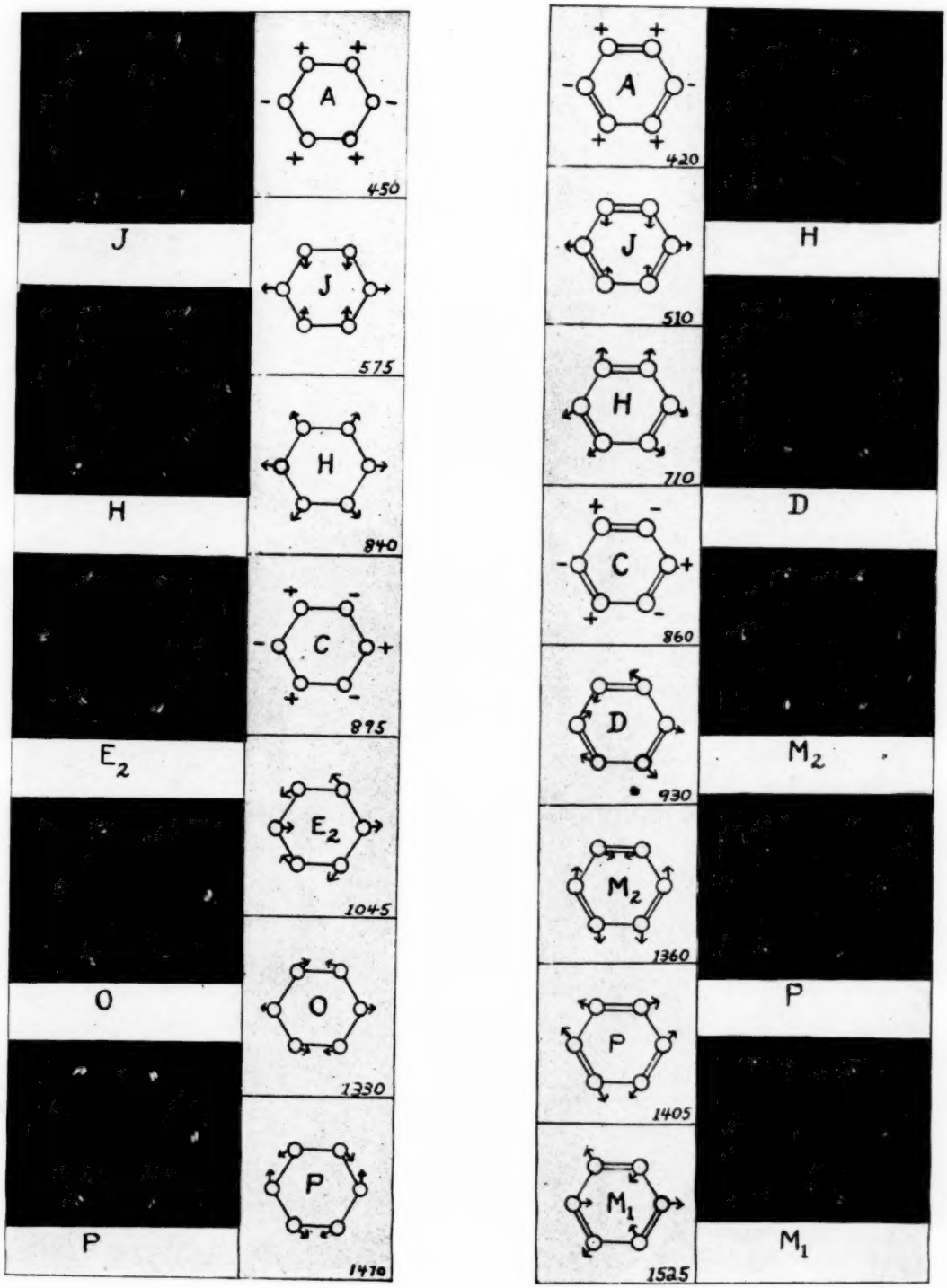

FIG. 1. Photographs of model motions in benzene. (a) Resonance formula; (b) Kekulé formula.

observing the vibrations of the models was also the same, with the addition in some cases of the photographic method described by Andrews and Murray.[2]

A change was made in the structure of the benzene ring used in the models. The recent work of Pauling[3] and Wheland has supported a structure for the benzene ring in which adjacent carbon atoms in the ring are joined by bonds about one and one-half times as strong as the normal carbon—carbon bond. It appears that the forces between atoms *meta* or *para* to one another are negligible. On the basis of these considerations the model used in this work was constructed with springs, joining adjacent carbon atoms, of a strength roughly one and one-half times that of the springs previously used to represent the normal C—C bond.

Although the previous investigations with the models indicated that there was great instability in the type of model representing the resonance formula for benzene, there appeared to be some hope that the addition of several heavy substituents around the ring would act as a stabilizing influence. This was found to be the case and fairly satisfactory results were obtained for most of the modes of motion. It was necessary, however, to leave off the balls representing the hydrogen atoms in order to avoid the complications of harmonics.

The first step in the investigation was therefore the study of the model of the "resonance" ring without hydrogens. This was carried out with the help of the photographic method[2] and since a model of the Kekulé formula for benzene was available it was studied at the same time. The results are shown in Figs. 1a and 1b. Photographs are included to show the motions which take place in the plane of the ring. The figures in the lower right-hand corner of each diagram are the r.p.m. at which the motion in question is observed.

More or less by chance the values of the r.p.m. correspond roughly to the values of the wave numbers in cm^{-1} so that comparison with the spectra is quite easy. One notes immediately that the frequencies of the two models cover about the same range, 400–1500. This is the range to which the vibrations of the ring have been assigned on the basis of the Raman and infrared spectra of benzene.

It is interesting to note that the frequency of the *P* type of vibration undergoes a change of less than five percent when the bonds are changed from the "one and one-half" type to alternate single and double. This weakens the argument that double bonds must be necessary to produce a frequency as high as the 1585–1606 cm^{-1} doublet in benzene, a hypothesis that certain authors have advanced. In fact the general distribution of frequencies for the two models is so nearly the same that it is useless to try to distinguish between them with the present accuracy of observation.

Fig. 2 shows the results obtained with the

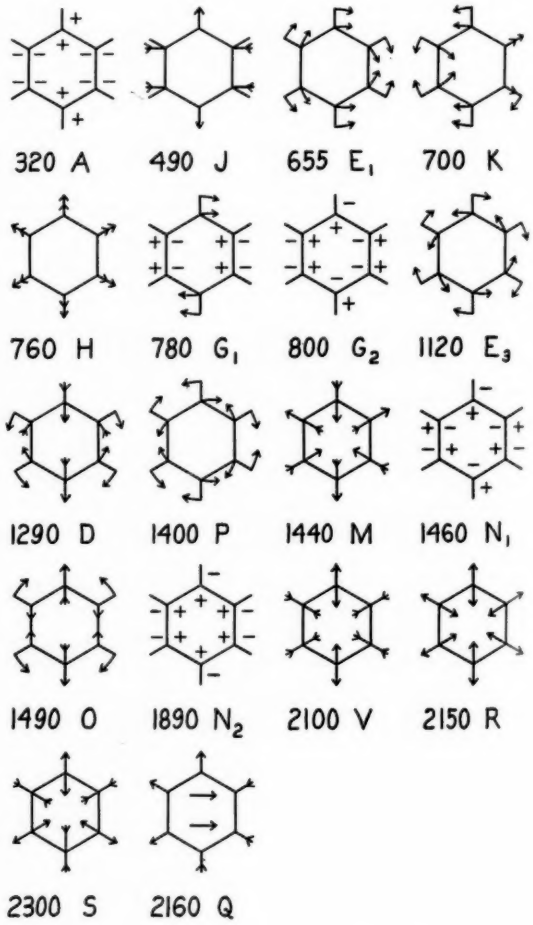

FIG. 2. Benzene, resonance formula.

[2] D. H. Andrews and J. W. Murray, J. Chem. Phys. **2**, 634 (1934).

[3] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

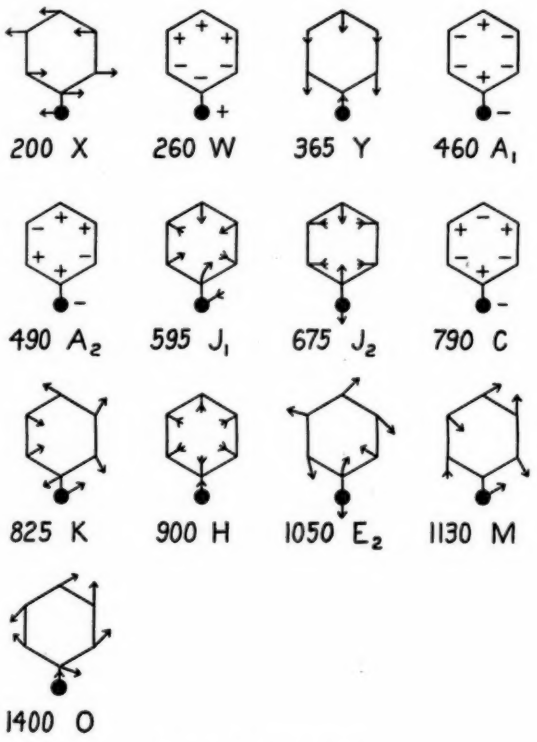

FIG. 3. Chlorobenzene.

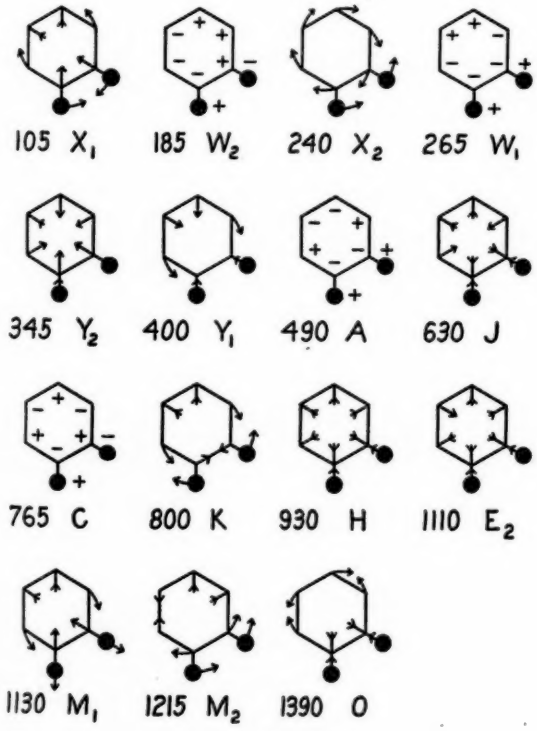

FIG. 4. *o*-Dichlorobenzene.

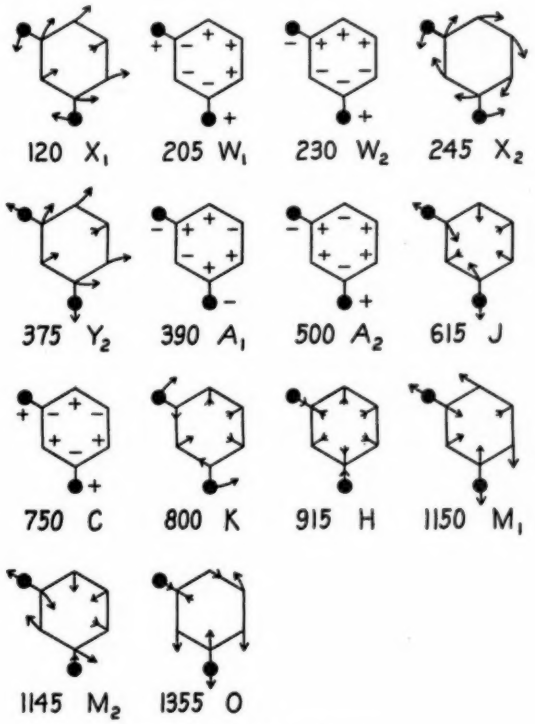

FIG. 5. *m*-Dichlorobenzene.

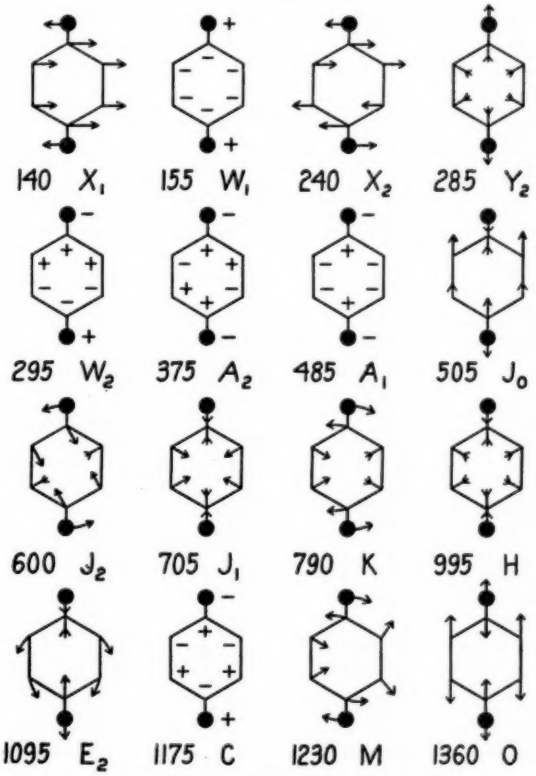

FIG. 6. *p*-Dichlorobenzene.

Pauling formula for benzene when balls and springs are added to represent the hydrogen atoms and C—H bonds. We do not believe these results are complete. From the mechanical point of view the Pauling ring structure is much less compact than the centric formula on which the earlier model was based.[1] As a result, there is much greater difficulty in getting clear-cut resonance in a steady state. Interference develops with harmonics and with types of motion possessing nearly similar frequencies and the results for that reason are much less certain.

On the whole the accuracy is again not great enough so that one can come out positively in favor of this Pauling formula. It is clear, however, that the change from the diagonal cross-bond structure to the Pauling formula shifts the frequencies for various types of motion very markedly. We may be able to identify these types of motion with certain lines in the spectrum by the shifts which take place upon substitution and also by the polarization and intensity of the lines. If this can be done, then the value of the frequency will give a clear-cut answer regarding the nature of the formula. For example, the *J* type of motion has a frequency corresponding to about 1100 cm^{-1} in the diagonal cross-bond formula and 675 cm^{-1} in the Pauling formula (provided we accept the identification of the *H* motion with the 992 cm^{-1} frequency). If the *J* motion can be positively correlated with the 606 cm^{-1} Raman line, then it will be quite certain that there are no forces comparable to cross bonds.

The study of the various chloro-derivatives of benzene was carried out with the model of the ring based on the Pauling formula, leaving off the balls and springs representing the hydrogen atoms and C—H bonds. This was done to avoid the difficulties of harmonic interference previously mentioned.

The results are shown in Figs. 3 to 10. The value of the mechanical frequency in r.p.m. is given under each figure. These values are plotted in Fig. 11. A scale has been added for converting them to cm^{-1}, based on the correlation of the 992 cm^{-1} line in benzene with the *II* type of motion. The Raman spectra are shown by the customary graphical plot in Fig. 12. The values

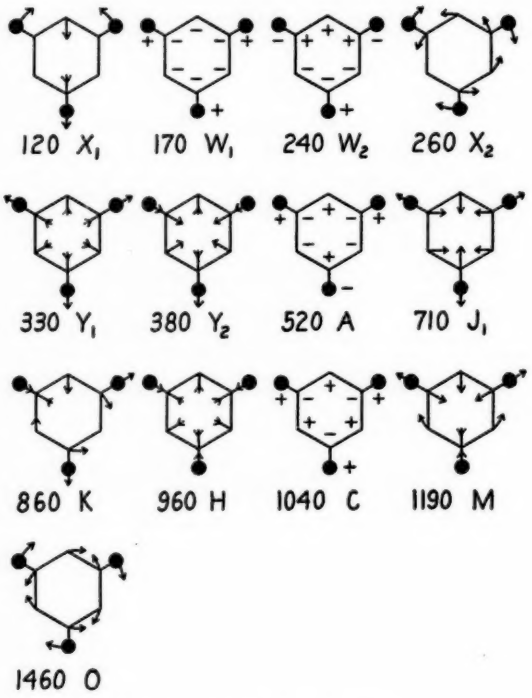

FIG. 7. 1,3,5-Trichlorobenzene.

for benzene are taken from the work of Grassmann and Weiler;[4] for C_6H_5Cl from Murray and Andrews;[5] for *o*, *m*, *p*-$C_6H_4Cl_2$ from Swaine and Murray;[6] for 1, 2, 3- and 1, 3, 5-$C_6H_3Cl_3$ from Kohlrausch;[7] and for 1, 2, 4-$C_6H_3Cl_3$ and C_6Cl_6 from Murray and Andrews.[8]

In comparing the model and Raman spectra one notes first of all the general similarity in the spectral region covered and in the number of lines for each compound. At least this is true for the compounds where it has been possible to get fairly complete Raman spectra. In the case of the higher melting compounds the fluorescence at high temperatures and the comparative insolubility have prevented the obtaining of satisfactory photographs. In the figure one notes the comparative paucity of lines in the spectra of

[4] P. Grassmann and J. Weiler, Zeits. f. Physik **86**, 321 (1933).
[5] J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).
[6] J. W. Swaine and J. W. Murray, J. Chem. Phys. **1**, 512 (1933).
[7] K. W. F. Kohlrausch, *Die Smekal-Raman Effekt*, Julius Springer, Berlin (1931).
[8] J. W. Murray and D. H. Andrews, J. Chem. Phys. **2**, 119 (1934).

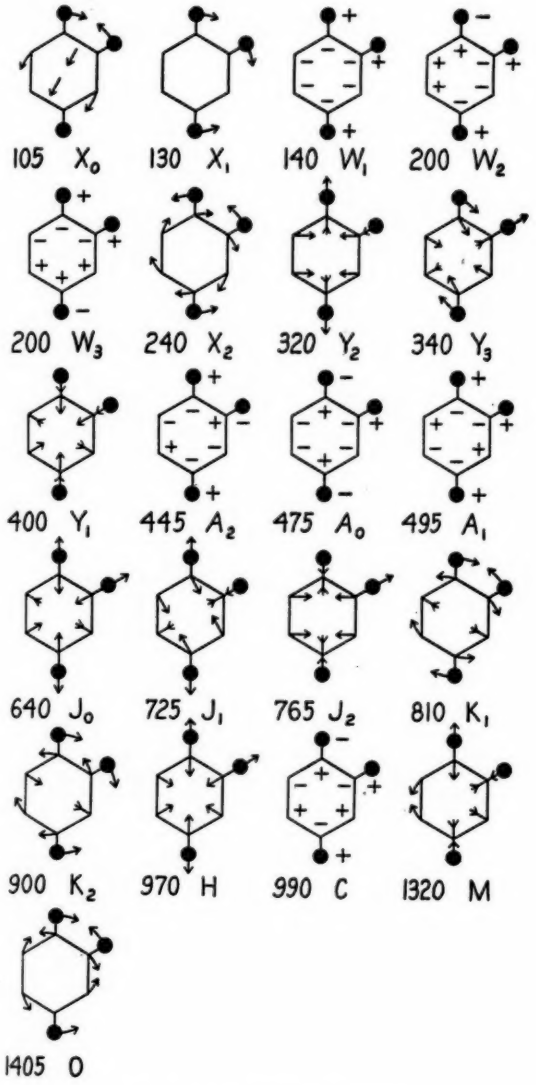

FIG. 8. 1,2,4-Trichlorobenzene.

1, 2, 3- and 1, 3, 5-$C_6H_3Cl_3$ and C_6Cl_6. Considerations of this sort led us to omit $C_6H_2Cl_4$ and C_6HCl_5 from the study.

As mentioned previously, the scale for comparing the model spectra with values of the frequency in cm^{-1} was calculated so that the line for the H type of motion in benzene falls at 992 cm^{-1}, the position of the strongest Raman line in benzene. There are two reasons for doing this. First, this line has been identified with the H type of motion by E. B. Wilson, Jr.,[9] on the basis

[9] E. B. Wilson, Jr., Phys. Rev. **46**, 146 (1934).

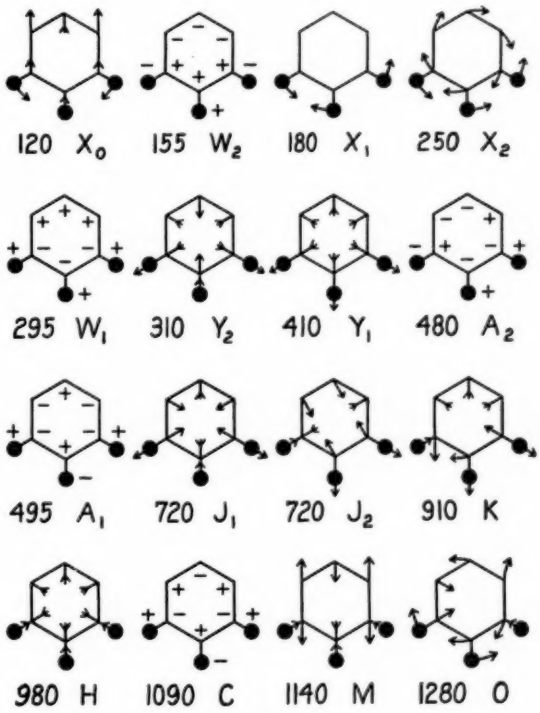

FIG. 9. 1,2,3-Trichlorobenzene.

of Placzek's selection rules for Raman spectra. In the second place, the series of model frequencies, associated with the H motion as we pass from C_6H_6 to C_6Cl_6, bears a striking resemblance to the series of lines in the Raman spectra which we obtain by selecting for each compound the strongest line found in the 1000 cm^{-1} region. The shifts in the model spectrum correspond to the shifts in the Raman spectrum, not only in sign but in magnitude.

This assignment of the 992 cm^{-1} line to the H motion does not correspond with the conclusions previously drawn by other authors. Kohlrausch[10] and his associates have attributed this line to a motion resembling the M_1 type in Fig. 1b. Bhagavantam[11] ascribes it to a type of motion like P in Fig. 1a. One notes, however, that neither the shifts of the M_1 line, nor those of P line in the model spectrum bear any resemblance at all to the shifts of the series of strong lines in the 1000 cm^{-1} region of the Raman spectrum. The

[10] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Sitzungsber. Akad. Wissensch. Wien [II b] **141**, 751 (1932).
[11] S. Bhagavantam, Ind. J. Phys. **5**, 615 (1930).

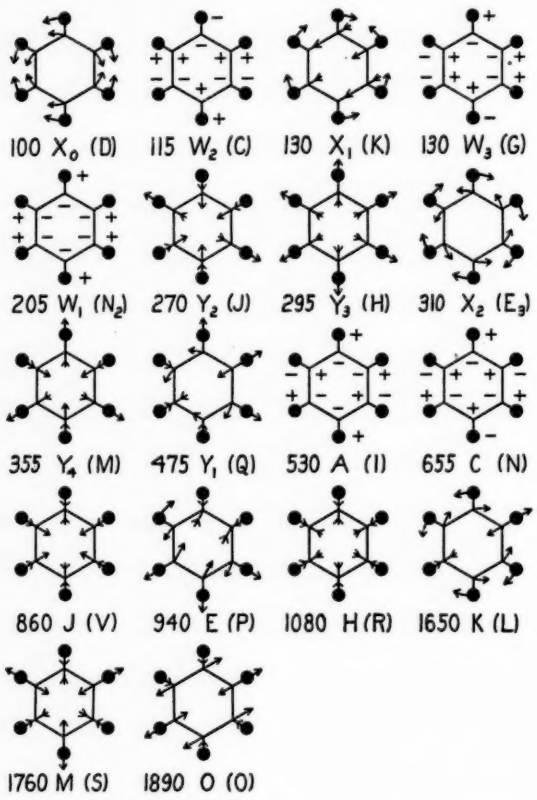

FIG. 10. Hexachlorobenzene.

striking resemblance of this series to the *H* frequencies and the lack of resemblance to any other set of frequencies make a strong argument in favor of this correlation. This is also in accord with the results found in the series of compounds studied by Teets and Andrews.[1] It agrees with the results obtained by Murray, Squire and Andrews[12] in their study of the shift of the 992 cm^{-1} line in passing from benzene to deuteriobenzene (C_6D_6).

Let us consider next the relations between the model and Raman spectra in the low frequency region where we find the motions associated with the substituent chlorine atoms. Quite apart from any arbitrary arrangement of the lines in series, we note the resemblance between the left-hand boundaries of the two figures. Except in the case of *p*-$C_6H_4Cl_2$ there is almost quantitative agreement between the lowest frequency found in the model spectrum of each molecule and the lowest line in the corresponding Raman spectrum.

The *X*, *Y* and *W* frequencies lying just to the right of the boundary also show some correlation between the two figures. As may be seen from Figs. 3–10, the *X* and *W* frequencies are associated with motions of the chlorine atoms bending the C—Cl bonds, in the plane of the ring for the *X* motion and perpendicular to the plane for the *W* motion. The *Y* motion takes place in the plane of the ring along the line of the C—Cl bond. In the case of C_6H_5Cl the correlation is quite good, if one neglects the two weak lines of zero intensity lying at 275 and 333 cm^{-1} which were not found by Dadieu, Pongratz and Kohlrausch.[10] In the other compounds it is much less certain. Lines have been drawn in, however, to indicate a few of the possible series relations in the Raman spectra.

Proceeding up the scale of frequency in the model spectrum we meet next the motions of type *A*, in which there is a bending of the ring perpendicular to its plane. This is the motion of lowest frequency in benzene. It is a type of motion that may be expected to have a very weak line according to the selection rules. As yet we cannot positively identify this series in the Raman spectra, although the "halogen" lines are in about the right place for this type of motion.

There seems to be more evidence for the next higher series, the one originating in the *J* motion in benzene. As previously mentioned, this series is important because it gives a clue to the strength of the forces between carbon atoms lying *para* to each other in the ring. In passing from benzene to chlorobenzene in the models the *J* motion which has a multiplicity of two in benzene, breaks down into two types of motion, in one of which the axis of symmetry includes the chlorine atom, while in the other it does not. At the same time the E_1 motion loses its identity and becomes coupled with one of these *J* motions. This is indicated by the dotted line in Fig. 11. Although the classification throughout the remaining members of the series is rather difficult, one finds some basis in the shifts in this region for assigning the lines to the *J* motions.

With the exception of the *H* motions which have already been discussed, there do not appear to be any other significant relations between the

[12] J. W. Murray, C. F. Squire and D. H. Andrews, J. Chem. Phys. 2, 714 (1934).

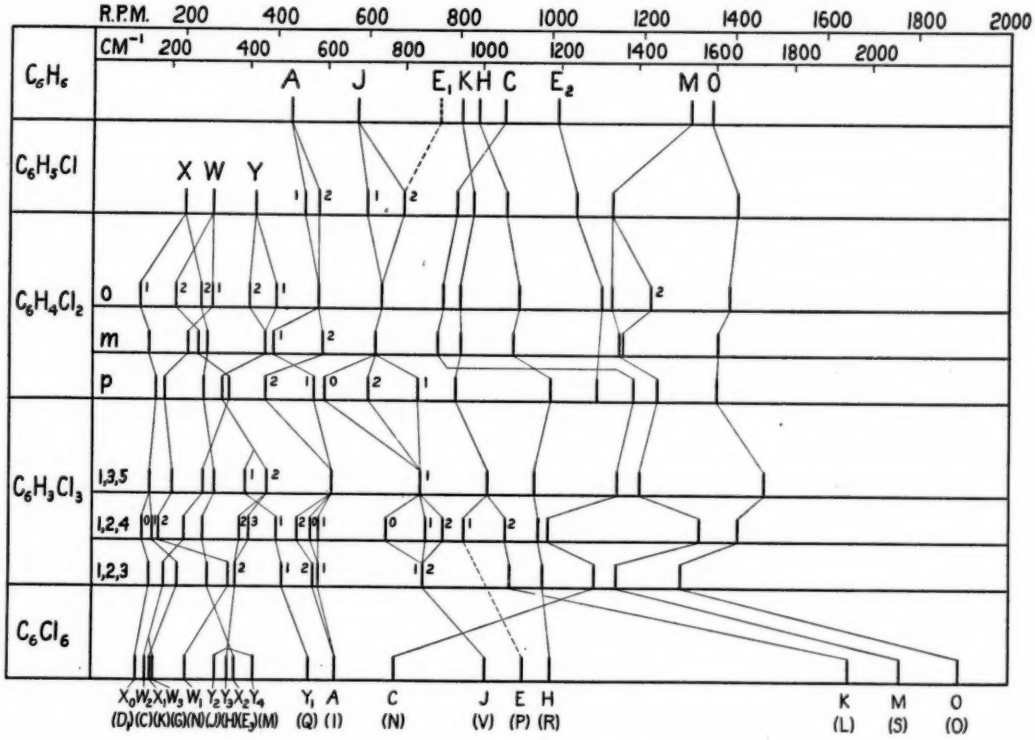

FIG. 11. Model frequencies.

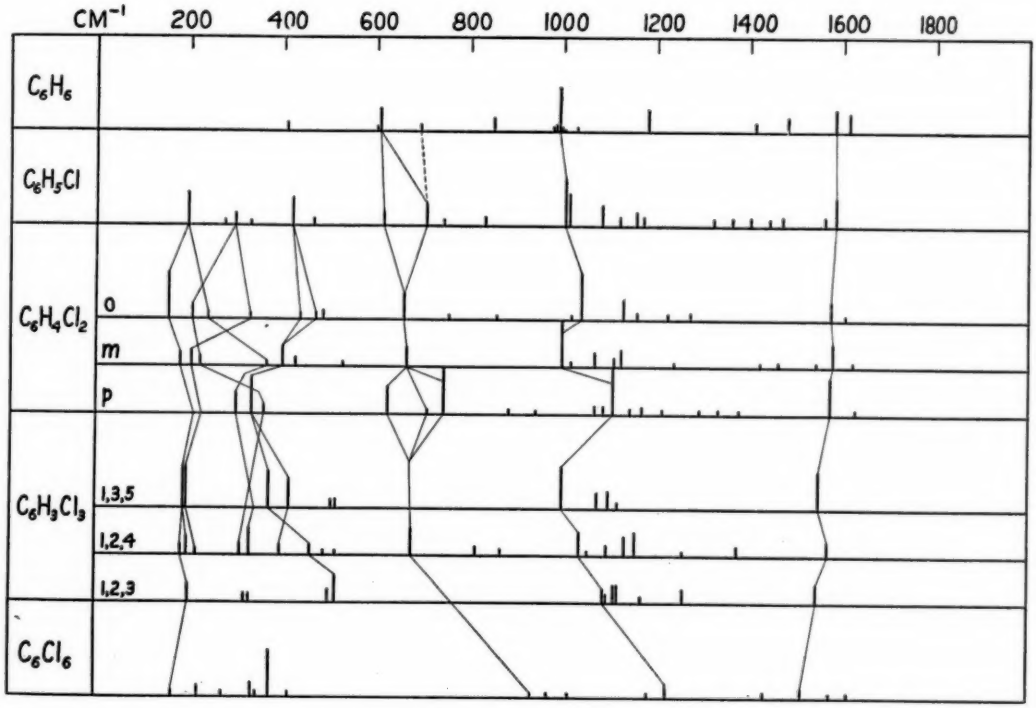

FIG. 12. Raman spectra.

models and the Raman spectra. The only lines in the spectra which appear to form a series are those lying beneath the 1600 cm^{-1} doublet in benzene. These lines form a kind of upper limit to the so-called "ring" region of the Raman spectrum. The *O*-series of model frequencies also forms the upper limit for the mechanical spectrum but the shifts in the two series are not at all the same. It will undoubtedly be necessary to have a very detailed knowledge of the ring forces and of the bending forces for the C−H bond before this region of the spectrum can be interpreted.

In closing we wish to call attention to the relation which the types of motion in C_6Cl_6 bear to the motions in C_6H_6. From the point of view of symmetry these two compounds are identical. Mechanically they differ in that benzene has the heavier of its two kinds of atoms in the ring while in C_6Cl_6 the substituent atoms are the heavier. We thus find two sets of relations between the motions in C_6Cl_6 and those in benzene. For example, the *H* motion, when traced through the series, ends up in a motion which generically speaking should be labeled "*H*," but is actually mechanically identical with the *R* motion in benzene. These two sets of relations are indicated by placing the generic symbol directly below the line in Fig. 11 while the symbol indicating the true mechanical counterpart of the motion in benzene is placed in parenthesis.

Because of these relations the motions in C_6Cl_6 may be compared with the motions deduced by E. Bright Wilson, Jr., for this symmetry class.[13] A diagram showing the character of these motions has been included in the preceding article of this series.[1] A comparison of these with the motions observed in C_6Cl_6 shows that in this model many of the predictions from group theory are confirmed.

[13] E. Bright Wilson, Jr., Phys. Rev. **45**, 707 (1934).

Finally let us sum up the evidence from these studies for or against the various formulas for benzene. The general agreement of the mechanical and Raman spectra indicates that the six carbon atoms in benzene are arranged in a flat ring and not in some other form such as a prism. The agreement of the positions and shifts of the *J* frequencies with the Raman spectra in the 600 cm^{-1} region indicates that there are no effective forces acting between carbon atoms para to one another in the ring, and is therefore evidence against the centric formula.

The 992 cm^{-1} series in the Raman spectra is identified with the *H* type of motion, from the shifts in the series of halogenated compounds and in deuterio-benzene. From this identification it is possible to calculate the average force constant of the C−C bond in the ring, obtaining a value of 7.55×10^5 dynes cm^{-1}, roughly one and one-half times the average value for the normal homopolar single bond. These facts are in accord with the resonance formula of Pauling or with the Kekulé formula.

The lack of extra lines in the Raman spectrum of the ortho-disubstituted compounds as compared with the para and meta is evidence that there are no isomers of the type to be expected on the basis of the stable Kekulé formula. One must conclude that, if molecules of the Kekulé formula exist, the transformation between the two isomeric forms is rapid compared with the frequency of 1000 cm^{-1}. It must be so rapid that the force effective in vibration of the ring is evenly distributed around the ring, so that the result is really the Pauling formula. The weight of evidence therefore seems to be in favor of the Pauling resonance formula for benzene.

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The Rotation of Molecules in Crystals

HARALD H. NIELSEN, *Mendenhall Laboratory of Physics, Ohio State University, Columbus*

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The problem of the rotation of molecules in crystals has been generalized to embrace also polyatomic configurations. Two models, of which the homo- and heteropolar diatomic molecules are special cases, are considered. The potential energy expressions are taken to be harmonic functions of the coordinates, satisfying the symmetry of the model under consideration. Two limiting cases exist; one where the crystal fields are small and effecting the motion of the top only slightly; the other where the crystal fields are large, restraining the top to rotate principally about its axis of symmetry, which will oscillate isotropically about its position of equilibrium. The eigenvalues of the problem are approximated for small fields by applying Schrödinger perturbation theory to the rotator and for large fields by applying Schrödinger perturbation theory to the isotropic oscillator in two dimensions. The connection of the eigenvalues for extreme values of the field is considered in detail. The eigenfunctions may on the rotator side be expanded in terms of the hypergeometric functions, and on the oscillator side in terms of associated Laguerre polynomials.

I. INTRODUCTION

THE interpretation of the specific heat measurements made on many crystals requires an assumption that there exists a critical temperature above which it is possible for the molecular configurations within the crystal to rotate. The problem has been discussed by several authors, but the only real attempts at a dynamical description of the phenomenon are those of Pauling[1] and Sterne[2] on rotation of diatomic molecules in crystals. While Pauling in reality treats the two dimensional model, Sterne has considered the actual three dimensional model of the spherical oscillator, pointing out that the Schrödinger equation is of the form of one of those encountered in studying the hydrogen molecule ion. Adopting a method for determining the eigenvalues for this equation developed by Wilson,[3] he is able to show diagrammatically how the energy level scheme varies as the crystal fields increase in magnitude.

While the problem of the spherical oscillator does not yield an exact quantum mechanical solution, the two limiting cases, where the crystal fields approach zero, thus effecting the motion of the top only slightly, and where the crystal fields approach infinity, so that the axis of symmetry oscillates isotropically about its position of equilibrium, are examples which may be solved exactly. These limiting cases shall henceforth be known as the *rotator* and *isotropic oscillator* sides respectively. The rather obvious implication is that the general case where the crystal fields take values intermediate between zero and infinity should lend itself to a solution by a perturbation method much like that used by Koenig[4] to solve Hill's equation. Since, however, no additional difficulties are encountered, the problem may as readily be generalized to embrace rotation also of polyatomic configurations in crystals. We shall, however, here confine ourselves to two particular polyatomic configurations which probably are among the most representative of those likely to rotate in the crystal form,[5] namely, the tetrahedral XY_3 configuration and the coplanar XY_3 configuration.

In Section II we shall adopt potential energy functions appropriate for our problem and set up the quantum mechanical Hamiltonian. In Section III we shall proceed to approximate the eigenvalues for the spherical oscillator in the region of small fields by applying Schrödinger perturbation theory to the limiting case of the rotator, the corresponding eigenfunctions being expandable in terms of the eigenfunctions of the symmetric rotator. In Section IV we shall develop asymptotic expansions to the eigenvalues in the region of strong crystal fields by applying perturbation theory to the other limiting case, the corresponding eigenfunctions here being expandable in terms of the eigenfunctions of the

[1] Linus Pauling, Phys. Rev. **36**, 430 (1930).
[2] T. E. Sterne, Proc. Roy. Soc. **A130**, 551 (1930).
[3] A. H. Wilson, Proc. Roy. Soc. **A118**, 628 (1928).
[4] Harold D. Koenig, Phys. Rev. **44**, 657 (1933).
[5] The homo- and heteropolar diatomic molecules in crystals may be thought of as special cases of these models, where the moment of inertia about the axis of symmetry has been shrunk to zero and where the angular momentum about this axis is zero.

isotropic oscillator in two dimensions. In Section V we shall consider the connection of the eigenvalues for extreme values of the crystal fields, while Section VI will be devoted to a discussion of the selection rules.

II. The Schrödinger Equation

In describing the motion of the top, it is customary to make use of two sets of coordinates; one set x, y and z fixed in space and another set, x', y' and z' fixed in the rotator. These two sets of coordinates may then be related to each other by the Eulerean angles θ, φ and ψ where θ denotes the angle between the space fixed z axis and the axis of symmetry z' of the top; φ denotes the azimuth angle and ψ the precession angle. The quantum mechanical expression for the kinetic energy of the rotator in these coordinates is well known, it having been determined by several writers.[6]

The potential energy function must represent some average value of the interactions of the rotator with the other components in the crystal lattice. It will in general be a function periodic in θ and φ, the periodicity being such that it will fulfill the symmetry requirements of the molecule; i.e., it must repeat itself every time the molecule assumes its initial position or one indistinguishable from it. We shall, in fact, assume that the potential energy function may quite well be represented by a sum of terms which are harmonic functions of the coordinates. The two particular models which we here wish to study, namely the tetrahedral XY_3 and coplanar XY_3 configurations will be referred to as model A and model B respectively[7] and their potential energy expressions will be considered individually.

Model A

The tetrahedral XY_3 configuration has the three Y particles located at the corners of an equilateral triangle and the X particle located at some distance d from their plane along the axis of symmetry. Referring this configuration to the Eulerean system it is seen that the required boundary conditions are: $V(\theta, \varphi)=V(\theta+2\pi, \varphi+2\pi/3)$. We shall adopt a potential energy function consisting of harmonic terms satisfying these conditions, breaking it off after the second term. Such a one is: $V(\theta, \varphi)=-2\mu_1 \cos\theta+\mu_2 \cos 3\varphi$, where μ_1 and μ_2 are parameters of magnitude depending upon the crystal fields. In this function the first term represents a torque restraining the top to rotate principally about its axis of symmetry while the second term limits the free rotation of the top also about z'.

Model B

The co-planar XY_3 model is a special case of Model A where $d=0$. Referring this to the Eulerean system one sees that because of its coplanarity, the required boundary conditions will this time be: $V(\theta, \varphi)=V(\theta+\pi, \varphi+\pi/3)$. A potential energy function broken off as before at the second term, made up of harmonic functions satisfying these boundary conditions may be taken to be: $V(\theta, \varphi)=\mu_1(1-\cos^2\theta)+\mu_2 \sin^2\theta \cos 2\varphi$, where as before μ_1 and μ_2 are parameters of magnitude. Here as before the first term depends only upon θ and seeks to make the rotator spin principally about its axis of symmetry while the second, a function of both θ and φ, limits the free rotation also about this axis.

It is now possible to write the complete quantum mechanical Hamiltonian. It is:

$$(1/\sin\theta)\,\partial/\partial\theta(\sin\theta\,\partial\Psi/\partial\theta)+(A/C+\cos^2\theta/\sin^2\theta)\partial^2\Psi/\partial\varphi^2+1/\sin^2\theta\,\partial^2\Psi/\partial\psi^2$$
$$-2(\cos\theta/\sin\theta)\partial^2\Psi/\partial\psi\partial\varphi+(8\pi^2A/h^2)\{E+\mu_1V_1(\theta)-\mu_2V_2(\theta, \varphi)\}\Psi=0, \quad (1)$$

[6] D. M. Dennison, Phys. Rev. **28**, 318 (1926); F. Reiche and H. Rademacher, Zeits. f. Physik **39**, 444 (1926); F. Reiche and H. Rademacher, Zeits. f. Physik **51**, 453 (1927); R. de L. Kronig and J. J. Rabi, Phys. Rev. **29**, 262 (1927); C. Mannebach, Phys. Zeits. **28**, 72 (1927).

[7] The regular tetrahedral XY_4 configuration is another typical case where rotation is apt to occur. This interesting model has its four Y particles at corners of a regular tetrahedron and its X particle at their center of gravity. It is especially interesting in that its symmetry prevents any definite choice of axis of symmetry. The potential energy function here must consequently depend upon both θ and φ, but contain no term in θ alone. In fact it is readily seen that a function conforming to the symmetry requirements for this model would be: $\mu_1 \cos\theta \sin^2\theta \sin^2\varphi$.

where A and C are the two principal moments of inertia (C being that about the axis of symmetry) and $V_1(\theta)$ and $V_2(\theta, \varphi)$ the two terms comprising the potential energy functions. Eq. (1), except for the last term ($\mu_2 V_2(\theta, \varphi)$) may become separable by the substitution:

$$\Psi = Y(\theta) \exp(i(K\varphi + M\psi)), \tag{2}$$

where as usual in such problems, the single-valuedness requirements demand that K and M be integers. In order to make (1) exactly separable, we make the restriction that μ_2 (i.e., the forces preventing free rotation about the axis of symmetry z') shall be small so that this term may be thought of as a perturbation term merely. While this limits the generality of the problem, it seems probable that in a great many cases the rotation about the axis of symmetry is only slightly restricted.

After substitution of (2) into (1) (where the term in μ_2 has been neglected) and dividing through by Ψ, we obtain as our unperturbed equation to be solved:

$$(1/\sin\theta)\, d/d\theta(\sin\theta\, dY/d\theta) + \{(8\pi^2 A/h^2)(E+\mu_1 V_1(\theta)) - K^2 A/C - (M - K\cos\theta)^2/\sin^2\theta\}\, Y = 0. \tag{3}$$

III. Characteristic Values and Functions Where μ_1 Is Small

In this section we shall approximate the characteristic values of Eq. (3) where μ_1 is small. We follow Sterne, making the following substitutions:

$$x = \cos\theta, \qquad \lambda^2 = 8\pi^2 A\mu_1/h^2, \qquad \Lambda = 8\pi^2 AE/h^2 - K^2(A/C-1) \quad \text{(for model } A\text{)},$$

$$\Lambda = (8\pi^2 A/h^2)(E-\mu_1) - K^2(A/C-1) \quad \text{(for model } B\text{)}.$$

in Eq. (3) and obtain:

$$(1-x^2)\, Y'' - 2x\, Y' + (\Lambda + \lambda^2 V(x) - (M - Kx)^2/(1-x^2))\, Y = 0. \tag{4}$$

When $\lambda = 0$, Eq. (4) reduces to the equation of the top, which when the substitutions:

$$Y = t^{a/2}(1-t)^{b/2}F, \qquad t = 1/2(1-x), \qquad a = |K+M|, \qquad b = |K-M|,$$

be made, may be written in the form of the hypergeometric equation. This has as a solution the hypergeometric function, and it may readily be shown that for this to be a suitable solution for the physical problem it is necessary that $\Lambda = J(J+1)$ where J is a positive integer. Thus, to obtain the eigenvalues of Eq. (3) when λ is a small quantity different from zero, we apply the Schrödinger perturbation theory to the equation of the rotator, interpreting $\lambda^2 V(x)$ as a perturbing potential which for models A and B will be, respectively, $((2)^{\frac{1}{2}}\lambda)^2 x$ and $\lambda^2 x^2$. The eigenvalues are evaluated to fourth approximation and the eigenfunctions to third approximation. The Schrödinger theory leads to the following well-known relations for the energies and the eigenfunctions:

$$E_k^{(n)} = \int H^{(n)} \Psi_k^{(0)} \bar{\Psi}_k^{(0)} dv + \sum_{i=1}^{n=1} \sum_{\tau=1}^{\infty} \int (H^{(n-i)} - E_k^{(n-i)}) A_{k\tau}^{(i)} \Psi_\tau^{(0)} \bar{\Psi}_k^{(0)} dv$$

and

$$\Psi = \sum_m \Big(\sum_s \lambda^{(s)} A_{km}^{(s)} \Psi_m^{(0)}\Big)$$

where

$$A_{k\tau}^{(i)}(E_k^{(0)} - E_\tau^{(0)}) = \int H^{(i)} \Psi_k^{(0)} \bar{\Psi}_\tau^{(0)} dv + \sum_{s=1}^{i-s} \sum_{j=1}^{\infty} \int (H^{(i-s)} - E_k^{(i-s)}) A_{kj}^{(s)} \Psi_j^{(0)} \bar{\Psi}_\tau^{(0)} dv.$$

For crystals belonging to model A, the problem is identically that of the Stark effect of polyatomic molecules. This has been discussed by Mannebach[8] who has carried the eigenvalues to second approximation. We restate his results, adding our own third and fourth approximations:

[8] C. Mannebach, reference 6. Mannebach has shown in this discussion of the Stark effect how the matrix components here encountered may readily be evaluated.

$$\lambda^2\Lambda^{(1)}{}_{J,K,M}=-\lambda^2KM/J(J+1), \qquad \lambda^4\Lambda^{(2)}{}_{J,K,M}=4\lambda^4(\Phi_{J,K,M}-\Phi_{J+1,K,M}),$$
$$\lambda^6\Lambda^{(3)}{}_{J,K,M}=64\lambda^6KM(\Xi_{J+1,K,M}-\Xi_{J,K,M}),$$
$$\lambda^8\Lambda^{(4)}{}_{J,K,M}=\lambda^8\{(32KM)^2(\Theta_{J,K,M}-\Theta_{J+1,K,M})+8(P_{J,K,M}-P_{J+2,K,M})\},$$

where:

$$\Phi_{J,K,M}=(J^2-K^2)(J^2-M^2)/(2J+1)(2J)^3(2J-1),$$
$$\Xi_{J,K,M}=(1/(2J-2)(2J)^2(2J+2))\Phi_{J,K,M},$$
$$\Theta_{J,K,M}=(1/(2J-2)(2J)^2(2J+2))\Xi_{J,K,M}, \tag{5}$$
$$P_{J,K,M}=((2J-2)/(2J)(2J-1))\Phi_{J,K,M}\Phi_{J-1,K,M}.$$

The coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the eigenfunctions up to third approximation have been computed, but will not be tabulated here since whenever they are needed they may quite readily be computed.

For crystals belonging to model B, the procedure is identically the same. The energies have been determined here also to a fourth approximation, but only three approximations are listed here since the fourth is entirely too long and unwieldy to be of interest. In this case also the coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the eigenfunctions will be omitted. The results are summarized below:

$$\lambda^2\Lambda^{(1)}{}_{J,K,M}=-\lambda^2\{\Phi_{J,K,M}+(KM)^2/J^2(J+1)^2+\Phi_{J+1,K,M}\},$$
$$\lambda^4\Lambda^{(2)}{}_{J,K,M}=8\lambda^4\{P_{J,K,M}-P_{J+2,K,M}+32(KM)^2(\Xi_{J,K,M}-\Xi_{J+1,K,M})\},$$
$$\lambda^6\Lambda^{(3)}{}_{J,K,M}=4\lambda^6\{(8KM)^2(R_{J,K,M}-R_{J+1,K,M})+(S_{J,K,M}-S_{J+2,K,M})$$
$$+(16KM)^2[((2J+4)/(2J+3))Q_{J+1,K,M}Q_{J+2,K,M}-2Q_{J,K,M}Q_{J+1,K,M}$$
$$+((2J-2)/(2J-1))Q_{J,K,M}Q_{J-1,K,M}]\}, \tag{6}$$

where:

$$\Phi_{J,K,M}=(J^2-K^2)(J^2-M^2)/(2J-1)(2J)^2(2J+1),$$
$$\Xi_{J,K,M}=(1/(2J-2)^2(2J)(2J+2)^2)\Phi_{J,K,M},$$
$$P_{J,K,M}=(1/(2J-1))(\Phi_{J,K,M}\Phi_{J-1,K,M}),$$
$$R_{J,K,M}=((\Lambda^{(1)}{}_{J-1,K,M}-\Lambda^{(1)}{}_{J,K,M})/2J)\Xi_{J,K,M},$$
$$S_{J,K,M}=((\Lambda^{(1)}{}_{J-2,K,M}-\Lambda^{(1)}{}_{J,K,M})/(2J-1)^2)P_{J,K,M},$$
$$Q_{J,K,M}=(1/(2J-2)(2J)(2J+2))\Phi_{J\,K,M}.$$

IV. Characteristic Functions and Values When μ_1 Is Large

It has been pointed out in Section I that when μ_1 is large we have what corresponds to the classical case of the rotator constrained to rotate primarily about its axis of symmetry, which in turn oscillates isotropically with simple harmonic motion about the space fixed z axis. Under these conditions the Eulerean angle θ will be small, and consequently we may replace the trigonometric function in θ in Eq. (3) by their expansions in terms of θ. Then making the substitutions:

$$x=(8\pi^2A\mu_1/h^2)^{\frac{1}{4}},$$
$$\epsilon^{(0)}=(8\pi^2A/h^2\mu_1)^{\frac{1}{2}}W=2(V+1), \tag{7}$$

where:

$$8\pi^2AW/h^2=8\pi^2AE/h^2-K^2A/C+16\pi^2A\mu_1/h^2, \quad \text{(for model } A\text{)}$$
$$8\pi^2AW/h^2=8\pi^2AE/h^2-K^2A/C, \quad \text{(for model } B\text{)}$$

and disregarding all but first order terms we have:

$$d^2Y/dx^2+(1/x)dY/dx+\{2(V+1)$$
$$-(L^2/x^2)-x^2\}Y=0. \tag{8}$$

Eq. (8) is the quantum mechanical equation for the isotropic oscillator in two dimensions, and has been carefully studied in connection with the carbon dioxide molecule by Dennison[9] who has shown that the solution must be of the form $Y(x)=\exp(-x^2/2)\ Z(x)$ where $Z(x)$ is the associated Laguerre polynomial which in order to remain everywhere finite requires that V must be an integer and that L take the values $V, V-2, V-4, \cdots$. This limitation on L leads in our problem to certain interesting relations between the quantum numbers K and M. We shall consider this point more in detail in Section V. The energy of the isotropic oscillator in two dimensions is then determined and by referring to (7) it is readily seen that for our problem it is:

$$E^{(0)}{}_{V,\,K}=(V+1)h\omega+K^2h^2/8\pi^2C,$$

where $\omega=(\mu_1/2\pi^2A)^{\frac{1}{2}}$.

To obtain asymptotic expansions for the eigenvalues where μ_1 is large we proceed to apply the Schrödinger perturbation theory to this limiting case, using as perturbation operators successively higher and higher order terms. To second approximation these are:

$$\lambda' H=(\lambda'/3)(xd/dx+(M^2+KM-2K^2)-ax^4),$$

$$\lambda'^2 H=(\lambda'^2/15)((x^3/3)d/dx+(M^2+7KM/4+K^2)+2bx^6/3),$$

where for model A, $a=1/4$, $b=1/16$ and for model B, $a=b=1$, and $\lambda'=(h^2/8\pi^2A\mu_1)^{\frac{1}{2}}$.

The procedure followed in obtaining eigenvalues and functions for model A, where the potential energy function is periodic in θ with a period of 2π, is identically the same as that of Section III.[10] The eigenvalues were actually evaluated to third approximation, but only the first and second are reproduced here, the third becoming entirely too unwieldy for use. Here as in Section III we shall omit the coefficients $A_{k\tau}{}^{(i)}$ in the expansions of the wave functions. The first and second approximations to the eigenvalues are given below:

$$\begin{aligned}
\epsilon^{(1)}{}_{V,\,L}&=(\lambda'/3)\{(M^2+KM-2K^2-1)-(1/4)(\alpha_{V+2,\,L}+(V+1)^2+\alpha_{V,\,L})\},\\
\epsilon^{(2)}{}_{V,\,L}&=(\lambda')^2\{(1/15)[((3V-3)/24)\alpha_{V+2,\,L}+((3V-7)/24)\alpha_{V,\,L}+(M^2+7KM+K^2-1/3)(V+1)\\
&\qquad+(V+1)^3/24]+(1/12)(\beta_{V,\,L}-\beta_{V+2,\,L})+(1/96)(\rho_{V,\,L}-\rho_{V+4,\,L})\},
\end{aligned}\tag{9}$$

where
$$\alpha_{V,\,L}=(V^2-L^2)/4,$$
$$\beta_{V,\,L}=((V^2-4)/4)\alpha_{V,\,L},$$
$$\rho_{V,\,L}=\alpha_{V,\,L}\alpha_{V-2,\,L}.$$

To approximate to the eigenvalues for model B where μ_1 is large, after the method we have been using, one should take into account that this model may oscillate isotropically about two positions of equilibrium, namely $\theta=\theta_0$ and $\theta=\theta_0+\pi$. Replacing θ by $\theta+\pi$ in Eq. (3) one sees that it again leads to Eq. (6) except that now L must be redefined as $|K+M|$. There will then be two independent solutions to the unperturbed Eq. (7) which we shall denote as $Y_{V,\,L}(x)$ and $Y_{V,\,L}(x+\gamma\pi)$ where $\gamma=2\pi(A\omega/h)^{\frac{1}{2}}$, corresponding to this twofold degeneracy. To obtain asymptotic expansions for the eigenvalues one should then use Schrödinger perturbation theory for degenerate systems; the first order perturbation contributions to the characteristic values occurring as roots of the secular determinant $|H^{(1)}{}_{k,\,l}-E\delta_l{}^k|=0$. The stabilized unperturbed wave function will then be seen to be $Y^{(0)}{}_{V,\,L}{}^i=(1/2)^{\frac{1}{2}}\{Y_{V,\,L}(x)\pm Y_{V,\,L}(x+\gamma\pi)\}$ where i takes values one and two, respectively, associated with the plus and minus signs.

Now in all cases except where either or both K and M are zero, will the above secular determinant yield identical roots so that in only a few cases will the degeneracies in θ be removed. This is readily seen since (1) by the symmetry of the problem, the two diagonal terms will be alike and, (2) the integrals which determine the values

[9] D. M. Dennison, Rev. Mod. Phys. **3**, 294 (1931).

[10] The matrix components here encountered have been evaluated by means of a method entirely similar to that used by Mannebach referred to under Section III. It is possible to expand $H^{(i)}\,Y_{V,\,L}(x)$ by means of a recurrence relation where the coefficients may be obtained by the method of undetermined coefficients.

of the non-diagonal elements will always contain periodic factors because of the restriction that $L=|K\pm M|$ which when integrated between the proper limits will vanish. Moreover since the wave functions have values only in the immediate neighborhood of $\theta=\theta_0$ and $\theta=\theta_0+\pi$, it is readily seen that for states where K or M are zero, the non-diagonal elements of the above determinant will be very small in the region of large μ_1. Hence the roots will also here be nearly alike; the splitting of the terms becoming appreciable only with increasing V and as μ_1 decreases to relatively small values. If we confine ourselves to the lower eigenvalues, i.e., for values of V not over two or three, we may to a good approximation ignore the splitting of the terms and here adopt a set of expressions similar to (9). For model B these are:

$$\begin{aligned}\epsilon^{(1)}{}_{V,\,L}&=(\lambda'/3)\{(M^2\pm KM+K^2-1)-(\alpha_{V+2,\,L}+(V+1)^2+\alpha_{V,\,L})\},\\ \epsilon^{(2)}{}_{V,\,L}&=(\lambda'^2)\{(1/15)[(2V+3)\alpha_{V+2,\,L}+(2V+1)\alpha_{V,\,L}+(M^2\pm 7KM/4+K^2-1/3)(V+1)\\ &\quad+(2/3)(V+1)^3]+(1/36)(\sigma_{V,\,L}-\sigma_{V+2,\,L})+(1/72)(\rho_{V,\,L}-\rho_{V+4,\,L})\},\end{aligned}\tag{10}$$

where α and ρ are defined as before and where $\sigma=(4V^2-1)\alpha_{V,\,L}$. The plus or minus signs are used accordingly as we define L to be $|K-M|$ or $|K+M|$. These expressions are similar to those developed by Wilson[11] and used by Sterne. These also show no splitting of the eigenvalues, but yield what might be termed mean values of the very closely lying components of the oscillator levels.

V. Connection of the Eigenvalues for Extreme Values of μ_1

Having now obtained expressions which approximate the eigenvalues in the region where μ_1 takes small values and asymptotic expansions for these in the region of large μ_1 values, it is possible to calculate and draw diagrams showing how these vary with μ_1. This has been done in Figs. 1 and 2 for models A and B, respectively. It is of interest, however, quite independently to investigate the connection of the eigenvalues for one extreme case with another, especially since it might serve to confirm our earlier work. It is possible to predict how this connection must take place by observing the nature of the degeneracies of each eigenvalue in the two limiting cases; by observing the restrictions placed upon the values of K, M and L for any value of V by the requirement of finiteness and by the relation $|K\pm M|=L$; and finally observing that Eq. (7) is of the Sturm-Liouville type with periodic coefficients concerning which, for given values of K and M, the oscillation theorem[12] states that the graphs of any two eigenvalues when plotted against μ_1 can never cross each other.

We consider first model A. In the extreme case of μ_1 equal to zero, the eigenvalues are those of the symmetric rotator and each is $2(2J+1)$ fold degenerate except for $K=0$ where the degeneracy is $(2J+1)$ fold. In the other extreme case where μ_1 is infinite, the eigenvalues are those of an isotropic oscillator plus a plane rotator. Now the requirement that the wave function remain finite fixes the values that L may take for a given value of V. Thus for example when $V=0$, L must also take the value zero. Hence by the condition $|K-M|=L$, K is always equal to M. Since, however, K (and M) may take either plus or minus values, all characteristic values where $V=0$ are twofold degenerate, except where $K=M=0$ which is single. Where $V=1$, L also must be unity, and the restriction $|K-M|=L$ establishes that $M=K\pm 1$. Thus since here again K takes either plus or minus values, eigenvalues with $V=1$ are fourfold degenerate. For higher values of V, analogous relations hold, so that in general we may say that any eigenvalue characterized by a quantum number V is $2(V+1)$ fold degenerate except where $K=0$ which has a $(V+1)$ fold degeneracy, and those where K assumes such values that $M=0$ which have a $(2V+1)$ fold degeneracy. Thus observing the requirements of the oscillation theorem that no two characteristic values of a given K and M

[11] A. H. Wilson, reference 3; T. E. Sterne, reference 2.

[12] E. L. Ince, *Ordinary Differential Equations*, p. 246.

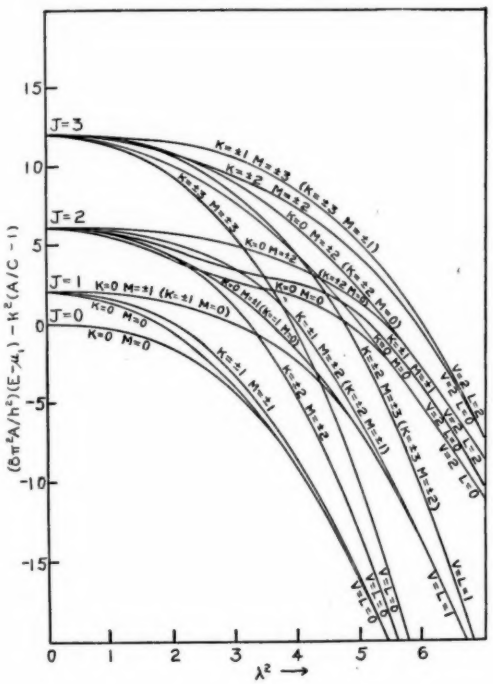

FIG. 1.

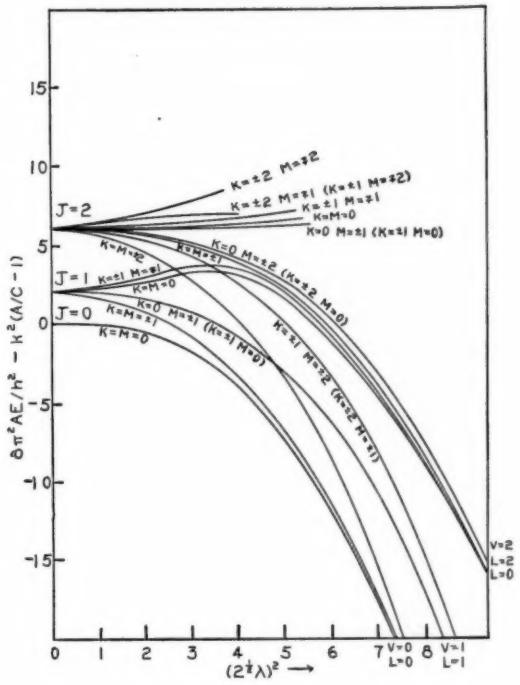

FIG. 2.

may ever cross, and observing that each component level in one limiting case must be consummated by one in the other limiting case, it is possible without ambiguity to join the eigenvalues in the two extreme cases. This is shown in Fig. 1.

For model B we proceed much as before. In the extreme case of $\mu_1=0$ the characteristic values are again those for the symmetric rotator with its characteristic degeneracies, and where μ_1 is infinite the eigenvalues are again those of the isotropic oscillator, but this time with somewhat different degeneracies. These differences, we know, arise because of the two positions of equilibrium $\theta=\theta_0$ and $\theta=\theta_0+\pi$, about which the molecule here may oscillate. Replacing θ by $\theta+\pi$ in Eq. (3) we have seen that L must be redefined as $|K+M|$. Thus taking for example $V=0$, and consequently also $L=0$, we have the restriction $K=\pm M$ always. Hence since K may take both plus or minus values, all levels where $V=L=0$ are fourfold degenerate, except in the instance where $K=M=0$ which is twofold degenerate. When for example, $V=1$ and $L=1$, this requirement becomes $K=\pm(M\pm1)$ and such eigenvalues, since K may take both plus and minus values will be eightfold degenerate except when $K=0$ which is only fourfold degenerate, and for such cases where K takes a value making $M=0$, which are sixfold degenerate. In general one may say that on the oscillator side, characteristic values have a degeneracy of $4(V+1)$ except those where $K=0$ which are only $2(V+1)$ fold degenerate, and those where K takes such values that $M=0$ which are $2(2V+1)$ times degenerate. As before, observing the oscillation theorem and noting that all component levels in each limiting case are accounted for, one may as before without ambiguity join the characteristic values of the extreme case of $\mu_1=0$ to those of the other extreme case of $\mu_1=\infty$. It is shown in Fig. 2 how these join.

VI. Selection Rules

We conclude our discussion of the spherical oscillator with a few remarks concerning the selection rules and the transition probabilities. Formally these may of course be determined in the usual manner by examining which of the matrix components are different from zero, but

since the problem is not exactly soluble, a general formulation cannot readily be given. By again considering limiting cases, however (i.e., where $\mu_1=0$ and where $\mu_1=\infty$) and observing how the characteristic values in these limiting cases connect, it is possible to predict which transitions will be the important ones.

A matrix component $q_{k,\,l}$ may be determined from the integral $q_{k,\,l}=\int\Psi_k q\Psi_l dv$ where q is the classical coordinate, Ψ_k and Ψ_l are the wave functions of the k-th and the l-th states, respectively, and dv is an element of volume in configuration space.

Kronig and Rabi[13] have considered the matrix components for the symmetric rotator (i.e., our problem where $\mu_1=0$) and have found that for the electric moment parallel to z', these vanish always except where $\Delta J=\pm1$, or 0; $\Delta K=0$; $\Delta M=\pm1$, or 0; and for the electric moment in the $x'y'$ plane they vanish unless $\Delta J=\pm1$, or 0; $\Delta K=\pm1$; $\Delta M=\pm1$, or 0.

We wish also to consider them when $\mu_1=\infty$. Our problem differing from that of Kronig and Rabi only in that the potential energy function is here different from zero the classical coordinates will be identically those used by them, which as is well known, are expressible in terms of trigonometric functions of the Eulerean angles. When $\mu_1=\infty$, θ, however, will be small so that we may as before replace the trigonometric functions in θ by their expansions in θ. Without actually setting up the integrals which lead to the matrix components, we shall state the results. When the electric moment is parallel to z', all matrix components will vanish except where $\Delta V=\Delta K=\Delta M=0$. When the electric moment is in the $x'y'$ plane, all matrix components are zero in first approximation unless $\Delta V=0$, $\Delta K=\Delta M=\pm1$. To investigate the selection rules to higher order approximations it is necessary to make use of the perturbed wave functions.

Now by referring to Fig. 1, it is seen that the only selection rule which remains of first order importance throughout all values of μ_1 when the electric moment is parallel to z', is the one $\Delta J=0$, $\Delta K=0$, $\Delta M=0$, where $J=K=M$. All matrix components arising from other transitions become of higher order importance only on the oscillator side, and as μ_1 becomes infinite go to zero.

When the electric moment is in the $x'y'$ plane, there are two sets of transitions of first order importance throughout all values of μ_1. These are $\Delta J=\pm1$, $\Delta K=\Delta M=\pm1$; $\Delta J=0$, $\Delta K=\pm1$, $\Delta M=\mp1$. All other transitions become of higher order importance as μ_1 increases and in the limit yield nothing.

These conclusions concerning the selection rules are strictly speaking, drawn from considerations of the limiting cases of model A only. Nevertheless these same are applicable also to model B since here again matrix components will vanish unless these are observed. This is true only insofar as transitions between levels characterized by solutions $Y_{V,\,L}(x)$ and $Y_{V,\,L}(x+\gamma\pi)$ may be neglected. These latter are however, of negligible significance in the region of large μ_1 and become of real importance only as the rotator side is approached. Even here these transitions in general offer no problem since as we have seen, only in the special cases where K or M are zero is this degeneracy removed so that transitions from an initial level to one component of a final level will be indistinguishable experimentally from transitions to both components or to the other component. Hence the same selection rules will be seen to be applicable to both models.

[13] Kronig and Rabi, reference 6.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Mixtures of Deuterium and Protium Oxides as Ideal Solutions

In several recent papers*[1] calculations have been made of equilibria involving the three forms of water molecules with the hydrogen isotopes of masses 1 and 2. In all such calculations it has been necessary to assume that in the liquid state the various species form ideal solutions. The only pertinent evidence is Luten's observation[2] that the molecular volume of mixtures of H_2O and D_2O does not vary linearly with the mole fraction, whence Luten deduces that the solutions are not ideal. However, the argument is not cogent since the existence of the intermediate molecule HDO introduces another variable and actually, if the molecular volume of HDO is assumed to be the geometric mean of the molecular volumes of H_2O and D_2O, one can deduce from equations of the type set out by Lewis and Cornish[3] that the square root of the molecular volume should vary as the mole fraction.

In order to obtain more direct evidence of the extent to which such mixtures deviate from ideal solutions it was decided to determine the composition of the vapor in equilibrium with mixtures of known composition. The method used was that employed by McBain, Pollard and Wynne-Jones[4] for determining the partial pressures of aqueous solutions of *p*-toluidine. The composition of the liquid was determined by means of a Pulfrich refractometer using a differential prism with which small differences of refractive index could be determined to 0.000005 of a unit. Since the difference in n_{20}^{D} between H_2O and D_2O is 0.00462[5] and Luten[2] has shown that the refractive index is a linear function of the mole fraction, the mole fraction could be determined to approximately 0.001. Duplicate experiments agreeing to this limit of accuracy were made with 10 and 50 percent D_2O and the results are given in Table I.

The last column gives the mole ratio of D_2O in the liquid divided by the value for the vapor.

On the assumption that $K=4$ for the equilibrium $H_2O+D_2O=2HDO$ and that $p_{HDO}=(p_{H_2O}p_{D_2O})^{\frac{1}{2}}$ it follows from the equations of Lewis and Cornish that for ideal solutions $R=(p_{H_2O}/p_{D_2O})^{\frac{1}{2}}$ and from the data of Lewis and MacDonald[6] the value of R should be 1.07. Topley and Eyring have calculated that the actual value of K is 3.26 but the introduction of this value instead of 4 has no perceptible effect on the result. The difference between 1.07 and 1.10 is definitely greater than the experimental error and the discrepancy may be the result of the assumption that p_{HDO} is the geometric mean of p_{H_2O} and p_{D_2O} or it may indicate a slight deviation from ideal behavior: in the latter event the activity coefficients need not differ from unity by more than 2 percent to account for the results. It is evident that these mixtures approximate rather closely to ideal solutions and that for most purposes no appreciable error is introduced by assuming ideal behavior.

TABLE I.

Liquid		Vapor		
Mole fraction	Mole ratio	Mole fraction	Mole ratio	R
0.1196	0.1359	0.1097	0.1232	1.10_4
0.4917	0.967	0.4667	0.8755	1.10_6

W. F. K. WYNNE-JONES

Frick Chemical Laboratory,
Princeton University,
February 1, 1935.

* Inter alia.

[1] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
Crist and Dalin, J. Chem. Phys. **2**, 735 (1934).
Farkas and Farkas, Trans. Faraday Soc. **30**, 1071 (1934).
[2] Luten, Phys. Rev. **45**, 161 (1934).
[3] Lewis and Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[4] McBain, Pollard and Wynne-Jones, Colloid Symposium **6**, 57 (1928).
[5] Taylor and Selwood, J. Am. Chem. Soc. **56**, 998 (1934).
[6] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 3057 (1933).

Note on the Crystal Lattice of Samarium Sulphate Octo-Hydrate

At the suggestion of Professor Ivar Waller of the University of Uppsala I undertook a determination of the samarium positions in the crystal lattice of the sulphate octo-hydrate. As the results may be of some value in connection with various paramagnetic problems, it was decided to publish the information obtained. Unfortunately it proved impossible to fix the positions of sulphur, oxygen and water because of the many degrees of freedom involved and also because of the small scattering powers.

The crystals used were borrowed from Dr. S. Freed of the Chemistry Department of this University.

The dimensions of the monoclinic unit cell were found to be: $a=20.30\pm0.06$A; $b=6.76\pm0.03$A; $c=13.53\pm0.05$A; $\beta=118°16'$. There are four molecules per cell and the space group is $A2/c(C_{2h}^{6})$. The eight samarium atoms are lying in general positions: $\pm(xyz)\pm(\frac{1}{2}-x, y, \frac{1}{2}-z)\pm(x+\frac{1}{2}, \frac{1}{2}-y, z)\pm(x, y+\frac{1}{2}, z+\frac{1}{2})$. Four of the sulphur atoms must lie on

the twofold axes, while all other atoms probably occupy eightfold positions. Disregarding the hydrogen atoms there are thus 37 degrees of freedom in the structure.

The determination of the three parameters for the samarium atoms was made by means of Laue photographs taken parallel to the c axis and perpendicularly to the c face. In this manner several hundreds of first order reflections were recorded.

For the great majority of reflections the observed intensity may be attributed to the samarium atoms alone. There are two reasons: In the first place the scattering power of samarium is great, and secondly, there are as many as 34 parameters for sulphur, oxygen and water, so that the chance of getting appreciable contribution from these atoms is small.

By using the data from the Laue photographs it was possible to fix the samarium parameters with considerable accuracy:

$x=0.106\pm0.003$; $y=0.025\pm0.006$; $z=-0.231\pm0.003$.

The closest distance between two samarium atoms is 5.08A. Around any given one of the samarium atoms there are 18 others at distances less than 10A, namely:

1	at 5.08A	2	at 7.08A
1	5.51	4	7.57
1	6.13	1	9.10
1	6.48	3	9.12
2	6.76	2	9.16

A great many of the lanthanides form octo-hydrated sulphates which are isomorphous with the samarium salt. As the axial ratios change very little throughout the series, the interatomic distances can be calculated with sufficient accuracy from the known distances in the samarium compound and the molecular volume. Thus the distances in the gadolinium salt are 0.2 percent smaller than in the samarium compound, in the erbium salt 1.1 percent smaller and in the neodymium salt 0.7 percent greater.[1]

W. H. ZACHARIASEN

University of Chicago,
February 4, 1935.

[1] The molecular volumes are given in G. v. Hevesy: Zeits. f. anorg. Chemie **147**, 217; **150**, 68 (1925).